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MINERALS AND MINERAL RELATIONSHIPS OF THE CLAY MINERALS*

By Clarence S. Ross

Preface

The invitation to be the Edward Orton, Jr., Fellow Lecturer of the American Ceramic Society for 1945 is a very great honor and a privilege which one interested in the mineralogy of clays must heartily appreciate. Dr. Orton was a geologist as well as a founder of this Society, and no doubt in issuing this invitation you had in mind the maintenance of this historic relationship. Those of us who follow him cannot add to that relationship, but I hope that I can help to foster it. Perhaps not all geologists know of this common ground between ceramics and geology as you do, and no doubt you would have me remind my geologic colleagues of this and of the mutual contributions which its maintenance entails.

Another common bond of interest is that ceramists have made use of mineralogic and petrographic techniques to an extent not matched in any other applied science. In particular, they have utilized the petrographic microscope, and ceramists and mineralogists alike have found in X rays a wonderful new method of research. Clays, the subject of this lecture, should provide a common meeting ground and one which no doubt would win the hearty approval of Dr. Orton.

I. Introduction

Clay mineralogy must begin with studies of selected pure materials, but should it stop with these, it would have but academic interest. However, the less pure clays which constitute soils and raw ceramic materials can be fully understood only when the individual minerals are known, together with their chemical and physical properties. Thus clay mineralogy becomes the first step in a very practical investigation.

The term clay has been used in varied senses, for instance, as the name for an unconsolidated rock, to designate a range of particle sizes, or to describe certain physical properties, most of these usages having a far from definite connotation. However, we are now concerned only with a group of specific minerals, which are the dominant components of clays, soils, shales, and related materials and which give these their characteristic properties.

Clay minerals have been defined as hydrous aluminum silicates, and minerals of this composition are those which characterize the group. However, studies of isomorphous groups have shown that nonaluminous members form a continuous series with some of the aluminous members, and so the entire series must be considered together. Thus we must include among the clay minerals some which otherwise would have been excluded from that grouping.

The clay minerals comprise three main groups, that is, the kaolin minerals, the montmorillonite group, and one that needs further study and that has received varied names, among which are hydrous micas and illite and *glimmerton*, of the Germans. All the minerals of these three groups are characterized by a sheet structure and so are related to the micas. The only others are allophane, without crystal structure, and a mineral with chain structure like the amphiboles which has been called attapulgite.

Clay minerals were long neglected by students of mineralogy. This was in part unavoidable since early methods for establishing the purity of such materials were inadequate and since impure as well as pure materials were analyzed. Many names were proposed, some of these based on chemical analyses made on impure samples, and names were commonly duplicated. However, most of the names now accepted for clay minerals were proposed by early workers, and Dana[1] exercised remarkable judgment in ascribing species rank to the many names which had been proposed. Thus a partial knowledge of pure materials representing most of the clay minerals was established, but the mineralogic

* The Edward Orton, Jr., Fellow Lecture was presented Monday evening, April 16, 1945, at the Forty-Seventh Annual Meeting, The American Ceramic Society, Buffalo, N. Y. Published by permission of the Director of the United States Geological Survey.

Dr. Ross is Chief of the Section of Petrology, U. S. Geological Survey, Washington, D. C.; for a biographical sketch, see *The Bulletin*, **23** [8] 258–60 (1944).

[1] E. S. Dana, System of Mineralogy, 6th ed. John Wiley & Sons, New York, 1892.

methods available for studying fine-grained materials were so inadequate that the mineralogy of clays, soils, and shales involved much guesswork. For instance, although montmorillonite had long been a well-established mineral, the idea persisted that kaolinite was the typical clay mineral, and all sorts of assumed mixtures were postulated in an effort to make analyses fit assumptions. On the other hand, a group working on soils believed that soils were commonly composed of amorphous oxides and hydroxides of silica, alumina, and iron, although crystallinity was readily observable under the microscope. There was long a disinclination to believe that clays could be made up of definite minerals.

The perfection of improved methods of mineralogic research has encouraged investigations of the more difficult minerals and, in particular, of groups of related minerals. Thus clays came under renewed investigation about twenty years ago, and since then there has been a steady progress in their study.

The intensive study of the clay minerals as a comprehensive group was initiated in the laboratories of the U. S. Geological Survey and has continued to the present time. Soon after, many workers in this country and in Europe became interested and have made important contributions to the many phases of clay mineralogy. So many angles are involved in the study of a difficult and complex group like the clay minerals that progress would have been slow without such widespread contributions.

Some of those whose work demands more than passing mention are Earl V. Shannon of the National Museum, John W. Gruner of the University of Minnesota, R. E. Grim and associates of the Illinois Geological Survey, C. E. Marshall of the University of Missouri, W. P. Kelley and associates of the University of California, Paul F. Kerr of Columbia University, Ulrich Hofmann and associates of Germany, Martin Mehmel also of Germany, W. Noll, another German investigator, and Gunter Nagelschmidt of Rothamsted, England. Sterling B. Hendricks of the U. S. Department of Agriculture is a co-author with the writer on a detailed study of the montmorillonite groups of clay minerals, a paper now in the course of publication.

A discussion of clay minerals may be preceded by a brief consideration of the various techniques which are most useful in the study of clays and related materials. Chemical analyses have been and must always remain the first and most essential step in their study. However, analyses together with all other mineralogic studies must start with assurance of essential purity. The petrographic microscope has long been a highly prized instrument of research in the hands of mineralogists, and by the use of chemical analyses, the microscope, and crystallography, Dick and Myers[2] gave us a nearly complete knowledge of the well-crystallized kaolin minerals over thirty years ago.

The petrographic microscope, however, did not reach its greatest usefulness in mineralogic studies until methods for the examination of mineral grains in immersion media were perfected. By this means, the purity of materials was more readily verified and analyses could be made with greater confidence.

The role of water in clay minerals has always presented a difficult problem since it is commonly present in two or more forms. Water as such may be present as adsorbed water and as interlayer water. So-called high-temperature water, or more properly (OH), as it is commonly represented in chemical analyses, is just one of the several oxide groups which form a definite part of the crystal lattice. Two methods of study of the various forms of water are available. In one, the sample is heated at constant temperature until repeated weighings indicate that it has reached equilibrium at that temperature; this is repeated at successively higher temperatures until all water is expelled. The results are then plotted as water loss against temperature, giving a curve of a type long in use.

The other is the differential heating method, first devised by Le Chatelier,[3] but recently perfected into an efficient self-recording instrument by Norton[4] and by Hendricks and Nelson and described in a paper by Hendricks and Alexander.[5] Grim and Rowland[6] have also published the results of clay studies by this method. The sample is heated at a constant rate and records any exothermic or endothermic reactions. This, or a simplified portable model, is proving very useful in the study of clays, bauxite, and related materials. Even the portable form devised for field use will detect 2% of gibbsite in kaolinite.

All who have to do with minerals are familiar with the application of X-ray methods to the study of crystalline materials. The lack of any external form, the exceeding fineness of grain, and the wide variation in composition in most clay minerals present problems which were solved only by X-ray methods. The relations of the clay minerals to one another and to other platelike minerals, the role of the different ions in the crystal structure, and the proxying of one ion by another were finally determined by X-ray technique.

The electron microscope has some inherent limitations as an instrument of mineralogic investigation; but the very fine grain and ready dispersability of the clay minerals gives it a usefulness in their study, and it has contributed some pertinent information about some of the clay minerals. Shaw and his associates[7] have shown that halloysite is characterized by elongated, bladed crystals and that the pseudohexagonal habit of

[2] (*a*) A. B. Dick, "Supplementary Note on the Mineral Kaolin," *Mineralog. Mag.*, **15,** 127 (1908).
(*b*) A. B. Dick, "On Kaolinite," *ibid.*, **8,** 15–17 (1888).

[3] H. Le Chatelier, "De l'action de la chaleur sur les argiles," *Bull. soc. franç. minéral.*, **10,** 204–11 (1887).

[4] F. H. Norton, "Critical Study of the Differential Thermal Method for Identification of the Clay Minerals," *Jour. Amer. Ceram Soc.*, **22** [2] 54–63 (1939).

[5] S. B. Hendricks and L. T. Alexander, "Minerals Present in Soil Colloids: I, Descriptions and Methods of Identification," *Soil Sci.*, **48** [3] 257–71, pl. I, II (1939); *Ceram. Abs.*, **19** [7] 173 (1940).

[6] R. E. Grim and R. A. Rowland, "Differential Thermal Analysis of Clays and Shales, a Control and Prospecting Method," *Jour. Amer. Ceram. Soc.*, **27** [3] 65–76 (1944).

[7] (*a*) B. T. Shaw and R. P. Humbert, "Electron Micrographs of the Clay Minerals," *Soil Sci. Soc. Amer. Proc.*, **6,** 148–49 (1941); *Ceram. Abs.*, **22** [10] 182 (1943).
(*b*) R. P. Humbert and B. T. Shaw, "Studies of Clay Mineral Particles with the Electron Microscope: I, Shapes of Clay Crystals," *Soil Sci.*, **52,** 481–87 (1941).
(*c*) B. T. Shaw, "Nature of Colloidal Clays as Revealed by the Electron Microscope," *Jour. Phys. Chem.*, **46,** 1032–43 (1942); *Ceram. Abs.*, **23** [4] 78 (1944).

kaolinite persists down to the finest fractions. Alexander and his associates[8] examined endellite and halloysite by means of the electron microscope and concluded that the bladed habit of halloysite is inherited from the endellite from which it is derived. In general, montmorillonite shows little or no characteristic form.

Color reactions have been found helpful in identifying clay materials. A number of organic compounds, in particular the aromatic amines and phenols, undergo a reaction which gives a color change in the presence of certain clay minerals. Eisenack[9] first described the method, and later Hendricks and Alexander[10] proposed the use of benzidine, of *o*-phenylene diamines, and of *p*-phenylene diamine, in particular recommending benzidine. Hauser and Leggett[11] also investigated reactions between clays and amines. Since 1937, benzidine (benzidine sulfate) has been used with varying success as an aid in distinguishing kaolinite from the montmorillonite type of clay. However, any soluble compound like iron or manganese salts which will oxidize benzidine will give purple or purplish-black colors, but with experience one will distinguish the blue color given by montmorillonite. For this reason, standardization with known materials is advisable. Thus the color reaction with benzidine will give useful results when used with caution, and, with some experience, will aid in clay identification. It has been used in clay prospecting and in evaluation of different beds in a clay pit.

II. Impurities

Clays are materials which are particularly subject to contamination with impurities, and their detection and the approximate determination of their proportions present a major problem in the study of clays. All shales and soils and most ceramic clays are mixtures of minerals, and so samples of even approximate purity suitable for mineralogic investigation are of exceptional occurrence.

The identity of many of the impurities in clays may be rather accurately determined. However, where essential amounts are present, where they are excessively fine grained, or where two or more clay minerals are present, the approximate estimation of proportions involves a rather large margin of error, even by the combined use of chemical analysis, X rays, petrographic examinations, and differential heating. This problem has been considered by Kelley and his associates[12] and by Hendricks and Alexander.[5]

The types of impurities, which must be determined to be absent, identified and removed if that is possible, or whose presence renders the material unsuitable for study, are extremely variable. Shales and soils in general contain such finely disseminated detrital minerals as quartz, feldspars, micas, carbonates, iron oxides, titanium in various forms, and a number of sparser minerals. Sedimentary kaolins may contain similar minerals, but the purer beds of commercial value are most apt to contain such minerals as quartz, micas, and, in some occurrences, gibbsite. Bentonites comprise the most widespread source of essentially pure montmorillonite, but Gruner[13] has shown that bentonites, particularly the soda bentonites, may contain cristobalite, and commonly the same type contains opaline silica. The included mineral grains of bentonites represent igneous rock phenocrysts and may commonly be removed by washing. Some clay materials may be purified by substituting sodium for calcium as the exchangeable base, and hence keeping the clay fraction in suspension, when this fraction may be decanted after long settling out of the nonclay fraction.

The impurities which may occur in clays are so varied that more than one method may be necessary for their detection. The kaolin minerals are the only ones whose chemical composition is so constant that variations from this can be accepted as an indication of impurities. All others may have a marked variation in the alumina-silica ratio and in accessory bases, and an excess SiO_2, Al_2O_3, etc., may be present without being indicated by chemical analysis. The various clay minerals have similar X-ray patterns, and the poor patterns, which they commonly give, are not always conclusive where more than one clay mineral is present. On the other hand, well-crystallized impurities are easily identified by X rays. The differential heating method is particularly useful for the detection of kaolinite, gibbsite, or montmorillonite and will also distinguish goethite, gypsum, diaspore, and boehmite, or the various carbonates.

The removal of iron oxides and hydrous oxides from clays without at the same time materially affecting the iron, which is an essential part of the crystal lattice, has presented a problem to those engaged in studies of soil materials. A method for this purpose has been perfected by Dion.[14]

The impurities in a large proportion of clay materials, the difficulty of a close determination of their proportions, and the way this has deterred mineralogists from undertaking clay studies have been mentioned. The question may still arise as to whether present-day methods permit the selection of materials of such purity

[8] L. T. Alexander, G. T. Faust, S. B. Hendricks, H. Insley, and H. F. McMurdie, "Relation of the Clay Minerals Halloysite and Endellite," *Amer. Mineralogist*, **28**, 1–18 (1943); *Ceram. Abs.*, **22** [5] 85 (1943).

[9] Alfred Eisenack, "Katalytische Einwirkung von Ionen und anderen silikatischen Mineralien und verbindungen auf aromatischen Amine und Phenole" (Catalytic Action of Clays and Other Silicate Minerals and Compounds on Aromatic Amines and Phenols), *Zentr. Mineral., Geol.*, **1938A**, No. 10, pp. 305–308; *Chem. Abs.*, **34** [7] 1976 (1940).

[10] S. B. Hendricks and L. T. Alexander, "Qualitative Color Test for the Montmorillonite Type of Clay Minerals," *Jour. Amer. Soc. Agron.*, **32** [6] 455–58 (1940); *Ceram. Abs.*, **19** [9] 223 (1940).

[11] E. A. Hauser and M. B. Leggett, "Color Reactions Between Clays and Amines," *Jour. Amer. Chem. Soc.*, **62** [7] 1811–18 (1940); *Ceram. Abs.*, **19** [11] 265 (1940).

[12] W. P. Kelley, W. H. Dore, A. O. Woodford, and S. M. Brown, "Colloid Constituents of California Soils," *Soil Sci.*, **48** [3] 201–55 (1939); *Ceram. Abs.*, **19** [5] 125–26 (1940).

[13] J. W. Gruner, "Cristobalite in Bentonite," *Amer. Mineralogist*, **25**, 587–90 (1940); *Ceram. Abs.*, **20** [4] 102 (1941).

[14] H. G. Dion, "Iron Oxide Removal from Clays and Its Influence on Base-Exchange Properties and X-Ray Diffraction Patterns of Clays," *Soil Sci.*, **58** [6] 411–24 (1944).

as to yield precise mineralogic studies. Clays derived from detrital materials commonly contain more than one clay mineral and are not suitable sources of pure minerals, but some mineral veins and, in particular, bentonites provide much more suitable materials. The derivation of the montmorillonite of bentonites from the single homogeneous material, volcanic glass, is particularly favorable for the production of a pure mineral. The mode of formation and tests from microscopic, X-ray, and thermal studies combine to indicate that materials with negligible amounts of impurities may be secured by means of careful coordinated tests.

An exceptional specimen which carried an undesirable proportion of impurities that had escaped detection would not vitiate final results of a mineralogic study of mineral groups. No careful mineralogist would attempt to base studies of a complex mineral group on a limited number of samples. Only by use of a large number of samples (50 to 100) may reliable results be attained.

Modern X-ray studies have given definite information about the crystal lattice of minerals and of the ions which may take positions in that lattice. Thus definite limits are imposed, within which variations of composition may occur. Mineralogic studies of a large number of minerals of the montmorillonite group have shown a definite trend of variations of composition which falls within the limits set by X-ray studies. Thus there seems to be ample evidence that means are available for the selection of materials whose purity is such that reliable results may be attained in mineralogical studies of the clay minerals.

Minerals with a sheet structure present the possibility of mixed layers, that is, the molecular sheets of two distinct types may form parts of a single crystal individual. Gruner[15] has presented evidence of mixed layers of vermiculite and biotite, and Hendricks[16] described mixed layers of vermiculite and chlorite. Potassium which runs to several percent in a few members of the montmorillonite group is, in general, nonreplaceable, in contrast with the replaceability of most of the sodium and calcium. The explanation of this seems to be the presence of mixed layers of muscovite or hydrous micas between some of the montmorillonite sheets.

III. Kaolin Minerals

The kaolin minerals, because of their simpler chemistry and better crystallization, present fewer and less complex problems than any other group of clay minerals; and their essential mineralogic relationships have been known for some time. The minerals of the group are kaolinite, halloysite, dickite, nacrite, endellite, and allophane. Kaolonite, halloysite, dickite, and nacrite have the same chemical composition and the same fundamental space lattice and differ only in the manner of stacking the lattice sheets one upon another. Halloysite and some kaolinite are so fine grained as to seem isotropic. Allophane is an amorphous material without an organized space lattice and its composition may vary within wide limits. Endellite, with twice the water of kaolinite, was first described in Germany and the name halloysite was redefined and transferred to it. This misapplication of names violated established rules of nomenclature, and the name endellite was proposed for the new mineral by Alexander and his associates.[8]

Anauxite, a material similar to kaolinite but with a higher proportion of silica, has presented a problem in mineral relationships, but it now seems probable that it is made up of kaolinite sheets with extra sheets of silica interspersed between those of kaolinite. It has been reported from only a few localities and has little importance.

Kaolinite, of course, is the member of the group with major economic interest. Dickite is of much rarer occurrence, but some deposits of possible usefulness are known. Halloysite is of widespread occurrence but in general forms deposits of limited size. However, it may form a minor constituent in kaolin deposits, and a few deposits have some potential value. Alexander and his associates[8] concluded that halloysite was a dehydration product of endellite, which had lost two molecules of water. However, halloysite from a number of localities has long been known which has a lower index of refraction than normal material and which seems to be intermediate between halloysite and endellite, perhaps with $3H_2O$.

Before the development of X-ray methods for the identification of clay minerals, it was assumed that all seemingly isotropic kaolin materials were halloysite. Later work, however, has shown that many of these materials were kaolinite in such a fine state of division that it is isotropic under the microscope. Allophane as far as is known forms only very small deposits of essentially pure material. However, the kaolinized feldspar in the vicinity of Roseland, Virginia, had a very low silica ratio, and this proved to be due to the presence of a large proportion of allophane.

The space lattice of the kaolin minerals is such that there is little substitution of ions in its structure. An iron-bearing kaolinite (faratsihite) has been described by Lacroix,[17] but re-examination by Hendricks[18] has shown that the material is a mixture of kaolinite and nontronite, and this is confirmed by differential heating tests. The same author concludes that there is no proxying of alumina by iron in kaolinite. The constancy with which the chemical analyses of kaolinite correspond to the theoretical formula $[Al_2Si_2O_5(OH)_4]$ indicates that Al does not proxy Si as it does in other clay minerals. The space lattice of the kaolin minerals is such that there are no unsatisfied valences on the cleavage surfaces and hence there is no adsorption of exchangeable bases on these surfaces. The edge of the

[15] J. W. Gruner, "Structure of Vermiculites and Their Collapse by Dehydration," *Amer. Mineralogist*, **19**, 557–75 (1934); *Chem. Abs.*, **29** [6] 1751 (1935).

[16] S. B. Hendricks, "Crystal Structure of Vermiculite and Mixed Vermiculite Chlorites," *Amer. Mineralogist*, **23** [12] 851–62 (1938); *Ceram. Abs.*, **18** [4] 110 (1939).

[17] Alfred Lacroix, "Sur l'opale, et sur une novelle espèce minérale (faratsihite) de Faratsiho (Madagascar)," *Bull. soc. franç. minéral.*, **37**, 231–36 (1914).

[18] S. B. Hendricks, "Random Structures of Layer Minerals as Illustrated by Cronstedtite ($2FeO \cdot Fe_2O_3 \cdot SiO_2 \cdot 2H_2O$); Possible Iron Content of Kaolin," *Amer. Mineralogist*, **24** [9] 529–39 (1939); *Ceram. Abs.*, **19** [5] 124 (1940).

sheet will have unsatisfied valences, and there will be a tendency for exchangeable bases to be held on these edges. However, the area of the edge of the sheets is so small compared with the total area that exchangeable bases will be insignificant except where the material has been subjected to very fine grinding.[19]

One mineral which is widespread in kaolin deposits is inadequately known. This material forms twisted wormlike crystals with a habit similar to that of kaolinite in the same occurrence and commonly occurs intergrown with kaolinite in alternating platelike segments. However, it has a higher index of refraction and a birefringence near that of micas. The material has received a variety of names and has been considered to be a secondary mica. Galpin[20] concluded that it had a chemical composition differing from that of kaolin in having one less molecule of essential water. No material which is not intergrown with kaolinite has been secured for detailed study. Chemical analyses of the purest material available (about 60% pure) tended to confirm the conclusion of Galpin, but further studies are necessary before the character of the micalike mineral is definitely known.

IV. Montmorillonite Group

The clay minerals of the montmorillonite group presented some unusually difficult problems in mineralogical research since they are characterized by extreme fineness of grain, being made up of micaceous sheets, one molecular layer in thickness, and without exterior crystal form; they are extremely variable in chemical composition; water plays several roles in their constitution; and they show marked base exchange, a property which in itself has presented outstanding research problems. Only by a coordination of all available methods for mineralogic research has a definitive picture of the mineral relationships of the montmorillonite group been secured.

The relationships of ions within the crystal structure of montmorillonite, bravaisite, and related minerals and probably also of the micas make advisable the representation of the composition by a type of chemical formula which may need some comment. The unvarying constants in the lattice structure of these minerals are the number of ions in tetrahedral positions and the number of oxygen ions. This enables us to base all formulas on the number of these ions in the unit cell or the more convenient one-half cell; that is, the Si + tetrahedral Al must always equal 4 and O + OH must equal 12, and the maintenance of these constants in all formulas permits a ready comparison; variations in composition are sharply presented by formula (1) which represents an analyzed mica. Thus, the fractional numbers which this system introduces are designed to represent chemical compositions and become a help in the presentation of the relationship of ions within the crystal lattice. The method of calculating analyses of minerals is discussed in a forthcoming paper by Ross and Hendricks and in a paper by the same authors on glauconite.[21] In formula (1), the interlayer ions are written first, followed by the group occupying octahedral positions, that by the tetrahedral ones, and finally the O, OH, and F. In montmorillonite, the order is the same except that for convenience (Na, Ca) follows $(OH)_2$ and indefinite interlayer water represented as (Aq) is last.

The relationships of the montmorillonite group of minerals may be illustrated by comparing them with the micas, talc, and pyrophyllite, minerals also possessing a sheet structure and to which they are closely related. Formulas (2) for talc and (3) for pyrophyllite are given.

Muscovite $(K_{0.97}Na_{0.14})(Al_{1.76}Fe'''_{0.08}Fe''_{0.03}Mg_{0.12})(Al_{0.86}Si_{3.14})O_{10}(OH, F)_2$ (1)

Talc $Mg_3Si_4O_{10}(OH)_2$ (2)

Pyrophyllite $Al_2Si_4O_{10}(OH)_2$ (3)

Muscovite $KAl_2(AlSi_3)O_{10}(OH)_2$ (4)

Biotite $K(Mg, Fe)_3(AlSi_3)O_{10}(OH)_2$ (5)

It is known that there are three octahedral positions available within the crystal lattice, but a stable lattice structure exists when only two of these are occupied as a pyrophyllite. When Mg proxies Al, the three bivalent ions find a place in the crystal structure and a valence balance is maintained. There are no essential substitutions of Al for Si in tetrahedral positions of pyrophyllite and talc, and there is complete balance of valences within the lattice structure. The mica formulas are commonly represented by (4) and (5), together with formula (1), based on an analysis of a typical muscovite. In the micas, there is the same relation between two Al ions in muscovite and the three Mg^+ ferrous Fe ions in biotite as in pyrophyllite and talc. However, in the micas, having the ideal formulas cited, one of the four tetrahedral positions in the crystal structure is being occupied by Al; that is, Al proxies Si in one of these positions. The substitution of a trivalent ion for tetravalent Si leaves a valence deficiency of 1 that is balanced by the K ion which occupies a position between the lattice sheets and ties sheet to sheet.

In members of the montmorillonite group, the unsatisfied valence caused by substitution of ions within the crystal lattice is in general only about one third as great as in the micas. This valence deficiency may result from the substitution of ions of lower valency in either octahedral or tetrahedral positions, and bivalent Mg commonly proxies trivalent Al and trivalent Al proxies tetravalent Si. The montmorillonite end member of the group shows a minimum substitution of Al for Si and the essential substitution is Mg for Al.

Formula (6) is typical of montmorillonite. In the highly aluminous members of the group, essential amounts of alumina proxy silica in tetrahedral positions

[19] A. L. Johnson and W. G. Lawrence, "Fundamental Study of Clay: IV, Surface Area and Its Effect on Exchange Capacity of Kaolinite," *Jour. Amer. Ceram. Soc.*, **25** [12] 344–46 (Aug. 1, 1942).

[20] S. L. Galpin, "Studies of Flint Clays and Their Associates," *Trans. Amer. Ceram. Soc.*, **14**, 301–46 (1912); p. 307.

[21] S. B. Hendricks and C. S. Ross, "Chemical Composition and Genesis of Glauconite and Celadonite," *Amer. Mineralogist*, **26**, 683–708 (1941); *Chem. Abs.*, **36** [3] 724 (1942).

Montmorillonite $(Al_{1.66}Mg_{0.33})Si_4O_{10}(OH)_2Na_{0.33}$, Aq (6)

Beidellite $Al_2(Al_{0.33}Si_{3.66})O_{10}(OH)_2Na_{0.33}$, Aq (7)

and are known as beidellite; formula (7) is representative of this group.

A more aluminous member of the group, however, is possible since the Al ions in octahedral positions may exceed 2 (3 such positions being available) and beidellite of approximately composition (8) is known.

Ferric iron may proxy Al in octahedral positions in any proportion but cannot assume tetrahedral ones and so the ferric iron member of the group, nontronite, differs from montmorillonite and beidellite only in being characterized by iron and is represented by formula(9).

Another member of the group is saponite, a mineral characterized by Mg proxying Al in octahedral positions and having formula (10).

Beidellite $Al_{2.18}(Al_{0.66}Si_{3.14})O_{10}(OH)_2Na_{0.33}$, Aq (8)

Nontronite $Fe_2(Al_{0.33}Si_{3.66})O_{10}(OH)_2Na_{0.33}$, Aq (9)

Saponite $Mg_3(Al_{0.33}Si_{3.66})O_{10}(OH)_2Na_{0.33}$, Aq (10)

Within the montmorillonite group, there appears to be complete isomorphism between montmorillonite, beidellite, and nontronite, but only limited isomorphism between these and the magnesian member, saponite. The only members of the montmorillonite group which occur in conspicuous amounts are the aluminous members in which Al is the essential ion occupying octahedral positions and in which varying amounts of that ion proxy Si in tetrahedral positions. However, there are commonly minor but essential substitutions of Mg for Al and commonly also of Fe for Al. A very wide range of ions may proxy Al, and clays containing minor proportions of Fe‴, Mn, Li and major ones of Cr, Ni, and Zn have been observed. The proxying of Al or Si ions by others of lower valence leaves the valency of the lattice structure out of balance and this is compensated by interlayer, exchangeable ions. In general, these may be either Ca or Na, but Ca commonly predominates. Since Na is monovalent and Ca is bivalent, one half as much Ca as Na is required to bring about a balancing of the valency. For that reason, these balancing ions might be represented as (Na, Ca/2), but the relations will be understandable without this extra complication being included in each formula. The dominance of Ca in most montmorillonites is due to its preferential fixation where that ion is available. These ions are the replaceable bases which play so important a role in soil fertility and which exert a controlling effect on the physical properties of clays. Experimentally, a large number of ions, including hydrogen (giving acid clays) and organic ions, may be substituted for the naturally occurring ones. The order of replaceability has been found to be as follows:

$$Li < Na < H < K < Mg < Ca = Sr = Ba < Rb$$[22]

A very small proportion of Mg and even Al may be replaceable, but most of the Mg forms part of the crystal lattice. Lithium may act as a replaceable base in experiments but like Mg is a part of the crystal lattice in natural occurrences as it is in lithium-bearing micas.

These replaceable ions seem, in montmorillonite, to differ from the K of micas, in that K links one molecular sheet to its neighbor while the exchangeable bases in members of the montmorillonite group are linked to only a single surface. This means that they are free to hydrolyze and hence hold one or more water layers between the lattice sheets; that is, the physical properties of members of the montmorillonite group are due to the exchangeable bases which insure that there shall be a water film between each layer. The thickness of this water film varies with the humidity,[23] but under normal humidity the basal spacing is about 15 Ångstrom units. In general, K is not replaceable in clays, and it seems probable that in these it is locked between sheets as in the micas.

The two dominant exchangeable bases produce rather different physical effects on wetting. Calcium clays do not disperse as completely as do sodium clays. The calcium clays break down to finely granular aggregates and give a minimum of material in permanent suspension. On the other hand, sodium clays disperse so completely that they may give permanent suspensions of jell-like masses. The calcium clays may be caused to give permanent suspensions by treatment with a sodium salt followed by removal of all excess salts.

Analyses and X-ray studies indicate that sodium clays commonly carry an excess of silica, and this may be present either as colloidal material or as the form of SiO_2 known as cristobalite. Thus, in general, calcium bentonites are made up of a purer clay mineral than are sodium bentonites.

The variations in chemical composition of members of the montmorillonite group can be illustrated by citing a few representative chemical analyses and the mineral formulas calculated from these (Table I).

The octahedral ions of the montmorillonite group in general exceed the number given in the typical formulas and range from 2.05 to 2.14 in analyses (1) and (4). In analysis (6), the magnesian clay, it is given as 3.03, which is probably the result of a small amount of replaceable Mg because this cannot exceed 3 in the crystal lattice.

Formula (2) represents a clay in which there is little proxying of Si by Al in tetrahedral positions but an essential proxying of Al by Mg. .The seat of this valence deficiency within the lattice structure is shown very clearly in analysis (5), where the almost-total lack of Al, which can proxy Si, and the proxying of monovalent Li for bivalent Mg introduce the only factor which can account for the interlayer balancing and exchangeable Na. In analysis (3), on the other hand, there is a large proxying of Si by Al, and hence the tetrahedral group is the seat of the base exchange. In analysis (1), there is a proxying of ions of lower valence

[22] P. Schachtschabel, "Research on Sorption of Clay Minerals," *Kolloid-Beihefte*, **51** [5–7] 199–276 (1940); *Ceram. Abs.*, **20** [1] 26 (1941).

[23] Ulrich Hofmann and Wilhelm Bilke, "Über die innerkristalline Quellung und das Basenaustauchverm Ogendes Montmorillonite" (Intracrystalline Swelling and Base-Exchange Power of Montmorillonite), *Kolloid-Z.*, **77** [2] 238–51 (1936); p. 246; *Chem. Abs.*, **31** [17] 6147 (1937).

TABLE I

CHEMICAL ANALYSES OF MINERALS OF THE MONTMORILLONITE GROUP

	(1) Lemon, Miss.	(2) Tetillas, Mexico	(3) Canal Zone	(4) Spokane, Wash.	(5) Hector, Calif.	(6) Kearsarge, Mich.
SiO_2	50.37	52.09	44.02	40.72	55.86	42.78
Al_2O_3	17.11	18.98	28.90	4.96	0.13	6.44
Fe_2O_3	2.68	0.06	5.15	29.57	0.03	1.27
FeO	0.20		0.33	0.71		
MnO		0.06			None	0.12
MgO	4.59	3.80	0.50	0.74	25.03	24.78
LiO					1.05	
CaO	1.23	3.28	0.68	1.98	Tr	2.35
Na_2O	0.56		0.17		2.68	0.75
K_2O	0.09		0.50		0.10	Tr
TiO_2			0.53	0.02	None	
F					5.96	
H_2O-	12.29	14.75	18.64	15.46	9.90	13.96
H_2O+	10.93	7.46		6.66	2.24	7.90
	100.05	100.48	99.42	100.82	102.98	100.35
O = F					02.51	
					100.47	

(1) Lemon, Smith County, Mississippi: Unusually pure bentonite, cream colored; R. E. Stevens, analyst.
(2) Tetillas, Vera Cruz, Mexico: Pale pink bentonite with very low iron content; J. G. Fairchild, analyst.
(3) Ancon, Canal Zone, Panama: Brown clay containing organic matter which was evidently deposited in presence of organic acids; J. G. Fairchild, analyst.
(4) Spokane, Washington: Nontronite, pale yellow-green in color; J. G. Fairchild, analyst.
(5) Hector, California: Hectorite, pure white magnesian clay; R. E. Stevens, analyst.
(6) Kearsarge Mine, Michigan: Saponite; Helen E. Vassar,[24] analyst.

CHEMICAL FORMULAS OF MINERALS OF THE MONTMORILLONITE GROUP

(1) $(Al_{1.42}Fe'''_{0.16}Mg_{0.32})(Si_{3.87}Al_{0.13})O_{10}(OH)_2(Ca_{0.11}Na_{0.06})$, Aq

(2) $(Al_{1.62}Mg_{0.42})(Si_{3.94}Al_{0.06})O_{10}(OH)_2(Ca_{0.26})$, Aq

(3) $(Al_{1.80}Fe'''_{0.29}Fe''_{0.02}Mg_{0.05})(Si_{3.26}Al_{0.74})O_{10}(OH)_2(Ca_{0.07}Na_{0.01}K_{0.03})$, Aq

(4) $(Al_{0.06}Fe'''_{1.94}Fe''_{0.05})(Si_{3.55}Al_{0.45})O_{10}(OH)_2(Ca_{0.18})$, Aq

(5) $(Mg_{2.68}Li_{0.32}(Si_{3.95}Al_{0.05})O_{10}(OH)_2(Na_{0.37})$, Aq

(6) $(Fe'''_{0.08}Fe''_{0.03}Mg_{2.92})(Si_{3.40}Al_{0.60})O_{10}(OH)_2(Ca_{0.20}Na_{0.12})$, Aq

In both the tetrahedral and octahedral groups. In analysis (3), the number of replaceable ions indicated is unusually low, but this clay was evidently deposited in the environment of organic acids and no doubt would have given an acid reaction, that is, H should have been included among the replaceable ions. Analysis (6) represents a typical saponite in which essential amounts of Al proxy Si. Analysis (5) is especially interesting because of the marked change in physical properties resulting from a small change in the chemical composition and the ensuing relations of its ions. It differs from talc only in containing about 1% of Li, and the exchangeable base (Na), which is required to balance the valency. This results in the water layer between each molecular sheet giving a material with extreme dispersion into a very perfect gel. Thus the small chemical difference gives rise to a very extreme physical difference.

[24] Charles Palache and H. E. Vassar, "Some Minerals of the Keweenawan Copper Deposits," *Amer. Mineralogist*, **10**, 417–18 (1925).

V. Hydrous Micas (Bravaisite)

One of the most widely occurring groups of clay minerals has commonly been referred to as the hydromicas or as hydrous micas. Grim[25] has called the group illite, and the German mineralogists have used the very aptly descriptive term *glimmerton*. Mallard[26] has given the name bravaisite to the specific mineral similar to muscovite, but with approximately one half the K_2O which characterizes muscovite. The priority of the name bravaisite indicates the advisability of its acceptance for the specific mineral of this type and to which a large proportion of such clays correspond, at least in composition. However, much additional work remains to be done on the low-potash, micalike clay materials and in particular on those varying from bravaisite in composition. For this reason, it has

[25] R. E. Grim, R. H. Bray, and W. F. Bradley, "Mica in Argillaceous Sediments," *ibid.*, **22** [7] 813–29 (1937); *Ceram. Abs.*, **17** [4] 157 (1938).

[26] F. E. Mallard, "Sur le Bravaisite Substance minérale nouvelle," *Bull. soc. franç. minéral.*, **1**, 5–8 (1878).

TABLE II

CHEMICAL COMPOSITION OF CLAYS WHICH CORRESPOND WITH BRAVAISITE

	(1) Allier, France	(2) Tenn.	(3) Fithian, Ill.	(4) South Wales
SiO_2	51.4	55.67	51.22	56.40
Al_2O_3	18.9	20.37	25.91	31.01
Fe_2O_3	4.0	2.35	4.59	2.77
FeO		0.34	1.70	
MgO	3.3	4.05	2.84	1.42
CaO	2.0	0.83	0.16	0.17
BaO				0.10
K_2O	6.5	6.10	6.09	5.40
Na_2O		0.31	0.17	0.95
TiO_2		0.32	0.53	0.68
P_2O_5				0.24
SO_3				0.04
H_2O+		9.09	7.49	
H_2O-			1.45*	
Ignition loss	13.3			No data
F		0.74		
Total	99.4	100.17	100.70	99.18
O = F		0.31		
		99.86		

* Omitted.

Bravaisite formulas

(1) $(Al_{1.20}Fe'''_{0.22}Mg_{0.37})(Al_{0.21}Si_{3.69})O_{10}(OH)_2(K_{0.35}Ca_{0.39})$

(2) $(Al_{1.67}Fe'''_{0.10}Fe''_{0.02}Mg_{0.36})(Al_{0.68}Si_{3.32})O_{10}(OH)_2(K_{0.45}Na_{0.02}Ca_{0.11})$

(3) $(Al_{1.45}Fe'''_{0.23}Fe''_{0.10}Mg_{0.23})(Al_{0.56}Si_{3.44})O_{10}(OH)_2(K_{0.47}Na_{0.01}Ca_{0.02})$

(4) $(Al_{1.66}Fe'''_{0.21}Mg_{0.12})(Al_{0.36}Si_{3.64})O_{10}(OH)_2(K_{0.4.2}Na_{0.11}Ca_{0.02})$

(1) Type bravaisite: Found in coal and bituminous schists, Noyant, Allier Dept., France (see Mallard, footnote 26).

(2) Micalike clay mineral: In unusually pure Ordovician bentonite, Chickamauga Dam, Tenn.; analyses by F. S. Grimaldi, Chemical Laboratory, U. S. Geological Survey.

(3) Described by Grim (see p. 283 of footnote 25) as illite: Fine colloid fraction, Pennsylvanian underclay, near Fithian, Vermilion County, Illinois; analysis by O. W. Rees.

(4) Mica described by Nagelschmidt (see p. 297 of footnote 29): Main constituent of shales overlying coal in South Wales; W. N. Adams, analyst.

seemed advisable to use the name bravaisite for the specific micalike mineral, with approximately one half of the K which characterizes micas, and to retain a noncommital descriptive term like hydrous micas for the inadequately known ones pending the determination of definite relationships.

Hendricks and Fry[27] first recognized the micalike mineral in soils and in the potash-bearing bentonite, which occurs over wide areas of the Ordovician formation of the eastern part of the United States. The material has also been studied by Endell, Hofmann, and Maegdefrau[28] in Germany, by Grim[25] and his associates in the United States, and by Hendricks and Alexander.* The papers by Grim contain more data on this group than any others so far published.

Analyses published by Grim[25] and by Nagelschmidt and Hicks[29] and numerous analyses made in the laboratories of the United States Geological Survey show a striking tendency of the minerals of this group to correspond in chemical composition with bravaisite. Table II gives the chemical composition of representative analyses of clays which correspond to bravaisite.

The water was expelled at greatly varying temperatures in the foregoing analyses, which are therefore not comparable, and the water lost at low temperatures (Aq) has been omitted from the formulas.

The minerals of the bravaisite type are similar to the micas and members of the montmorillonite group in that Al partly proxies Si in tetrahedral positions and four of these positions must be filled for each one-half unit cell. As in the micas and montmorillonite, the ions in octahedral positions are also close to but not necessarily exactly 2 in members of the group made up dominately of trivalent ions, that is, of Al + Fe'''.

The ions in octahedral positions in typical hydrous micas are dominantly Al, with lesser proportions of ferric iron, ferrous iron, and magnesium. The role of Ca and Na in minerals of the bravaisite type is somewhat problematical, but they no doubt assume positions between the lattice sheets (as these are exchangeable), at least in part. However, the base-exchange capacity of the micalike clay minerals is much lower than in members of the montmorillonite group but higher than in kaolinite.

Clays of the bravaisite or hydrous-mica type characterize shales formed under marine conditions and are present in soils derived from such shales. The Ordovician bentonites are an outstanding example of this clay mineral. Thus, a clay mineral of the bravaisite or so-called hydrous-mica type may be expected to be dominant in a large proportion of the low-grade clays.

The most useful criteria for the recognition of the various types of clay minerals are outlined in Table III.

The indices of refraction of kaolinite and dickite are essentially the same, and under the microscope these minerals differ most markedly only in habit. Kaolinite tends to form twisted or curved, wormlike individuals.

[27] S. B. Hendricks and W. H. Fry, "Results of X-Ray and Microscopical Examinations of Soil Colloids," *Soil Sci.*, **29**, 457–78 (1930).

[28] Kurd Endell, Ü. Hofmann, and E. Maegdefrau, "Über die Natur des Tonanteils in Rohstoffen der Deutschen Zementindustrie" (Nature of Clayey Raw Materials Used in the German Cement Industry), *Zement*, **24** [40] 625–33 (1935); *Ceram. Abs.*, **15** [11] 346 (1936).

* See Hendricks and Alexander, footnote 8.

[29] G. Nagelschmidt and D. Hicks, "Mica of Certain Coal-Measure Shales in South Wales," *Mineralog. Mag.*, **26** [180] 297–303 (1942); *Ceram. Abs.*, **23** [11] 198 (1944).

TABLE III
DIAGNOSTIC PROPERTIES

Mineral	Habit	Indices of refraction α	Indices of refraction γ	Indices of refraction Mean	Birefringence	Optical character	Diagnostic tests
Kaolinite	Plates, forming curved groups; parallel extinction	1.560	1.566		0.006	(−)	X-ray or differential heating; optical tests usually sufficient
Dickite	Monoclinic, platy, inclined extinction	1.560	1.566		0.006	(+)	Some plates standing on edge show inclined extinction (15°–20°)
Halloysite	Conchoidal fracture; isotropic			1.552	None		X-ray, optical properties not conclusive
Micalike kaolin mineral	Platelike, parallel extinction	1.557	1.573		0.014	(−)	Intergrown with kaolinite, high birefringence
Bravaisite-type material	Micalike, parallel extinction	1.525	1.567		0.042	(−)	Resembles micas, essential K_2O
Bravaisite (Ordovician bentonite)	Platy, appears shredlike	1.535	1.565	1.555	0.03	(−)	Resembles montmorillonite; index of refraction higher; contains K_2O
Montmorillonite (low iron)	Very fine-grained shredlike, but clearly crystalline, occasional areas elongated plates	True mean index 1.53 With occluded air 1.47			0.03	(−)	Low index of refraction; high birefringence; very fine-grained; high water content
Montmorillonite (high iron)		True mean index 1.55 With occluded air 1.50			0.03	(−)	
Nontronite	Very fine-grained shredlike, but clearly crystalline, occasional areas elongated plates	True mean index 1.61 With occluded air 1.56			0.04	(−)	Low index of refraction; high birefringence; very fine-grained; high water content

Dickite commonly occurs as fine-grained aggregates of equidimensional grains, and where massive gives chert-like texture but with a higher relief. A few occurrences of dickite contain very perfect micalike crystal plates with a modified hexagonal outline. The inadequately known mineral of some kaolin deposits may be recognized by a much higher birefringence than that of the intergrown kaolinite. Halloysite has the mean characteristic index of refraction of the kaolin minerals but is definitely differentiated from submicroscopically crystalline kaolinite only by means of careful X-ray tests.

The differentiation of montmorillonite and the hydrous micas by microscopic methods is commonly difficult. The birefringence of the two groups is very nearly the same. The indices of refraction of montmorillonite are distinctly lower than that of the micas except in the members of the montmorillonite group, which are high in iron, when they may overlap those of hydrous mica. Attapulgite resembles hydrous micas when examined under the microscope but has a mean index of refraction of about 1.530. The X-ray and differential heating method, however, is probably the only definite means of identification. Allophane has a very low index of refraction (1.468 to 1.485); its isotropic character and high water content differentiate it from any other clay material and it would probably be confused only with opal. The indices of refraction of all clay minerals except the well-crystallized members of the kaolin group are variable, and the figures given in Table III are not invariable values.

VI. Geologic Relationships

The mineralogical identity and physical properties of the various clay minerals are a result of their geologic history; that is, their uses in industry and the role they play as soil-forming materials are the result of the physical and chemical environments through which they have passed in the course of their formation. Some pertinent information may thus be derived from a brief consideration of some of these relationships.

The physical-chemical system which controls the formation of a clay material may be conveniently considered in two parts, one, the chemical character of the parent material from which it was derived, and the other, the chemistry of the environment in which alteration takes place. Many clay materials have had so varied a history that the physical chemistry of the system or successive systems in which they developed are not readily determinable, but others have developed under conditions which yield some direct information about genetic processes.

Kaolinite is the highest-grade clay material for ceramic uses although perhaps others and of lower grade are more widely used. This usefulness of kaolin is the result of two factors: One is the high alumina-silica ratio and the other is the essential absence of iron and other bases in its chemical composition. Other clay minerals, particularly montmorillonite and the hydrous micas, are commonly iron bearing, for in these iron proxies alumina in the crystal lattice.

The tendency for kaolinite to form in an acid environment resulting either from humic acids or oxidizing sulfides has long been recognized. On the other hand, kaolinitic clays are also the result of strong leaching action where essentially neutral conditions seem probable and where acid reactions seem to be precluded. Both processes tend to remove bases from the system, and it seems evident that this, rather than acidity as such, controls the formation of kaolin minerals. That is, kaolin minerals form most readily in systems characterized by a minimum of available elements other than silica, alumina, and water. The alkalis of weathering

granites and pegmatites seem to have little effect on the process, or perhaps they favor the removal of excess silica.

Minerals of the montmorillonite group have been synthesized[30] in the presence of alkalis and alkaline earths but formed under the widest range of conditions in the presence of magnesium. The discussion of montmorillonite indicated the essential role of bases and in particular of MgO in their composition. However, it is probably not alkalinity but the presence of suitable bases which controls the formation of montmorillonite. Ferrous iron plays a role similar to that of magnesium in the formation of silicate minerals, and so the presence of reducing conditions, or those which were not actively oxidizing, would also tend to favor the formation of minerals of the montmorillonite group. Iron oxides and kaolinite, however, are commonly associated; in fact, deep red-soil materials are normally kaolinitic. This shows that kaolinite rather than montmorillonite forms in the presence of iron when that element is thoroughly oxidized to hematite. The formation of hematite probably removes iron from the reacting system almost as effectively as when it is removed by leaching.

The chemical factors mentioned indicate the reason for the formation of kaolinite from some parent materials and of montmorillonite from others. The weathering of rocks characterized by alkalic feldspars, especially of pegmatites and granites, tends to yield kaolinite, but rocks characterized by calcic feldspar may weather to montmorillonite. The hydrous micas and the clay materials of marine shales and limestones also tend to weather to kaolinite. Since kaolinite has small base-exchange capacity, it is unable to retain essential amounts of bases, and soils derived from limestones are commonly deficient in lime. Rocks characterized by calcium, magnesium, and iron tend to weather to montmorillonite or beidellite. Thus basalitic rocks tend to weather to a mineral of the montmorillonite type. This tendency, however, is affected by physical conditions; and when subjected to active oxidation and leaching, basalts may, on weathering, give kaolinitic soils. Glacial materials are very heterogeneous and commonly contain clay materials, which may be hydrous micas in addition to igneous rock minerals including feldspars, hornblende, etc., as also may calcium and magnesian carbonates. Such materials normally weather to montmorillonite minerals although, as in the weathering of basalts, strong leaching and oxidation would tend to favor the formation of kaolinite.

The derivation of bentonitic clay from glassy volcanic ash has long been recognized. The glass is believed to be in general of a composition which would give a feldspar-rich rock had it crystallized. Such glasses would be rich in alkalis and would contain Ca, Mg, and usually Fe in lesser amount. The alkalis and part of the silica are removed during the alteration of the glass to clay, but Mg, Fe, and Ca tend to become fixed.

The dominance of the hydrous-mica type of minerals in marine sediments has been mentioned. However, the products of land erosion, which formed the parent source of a large part of marine sediments, must have contained essential proportions of kaolinitic minerals and of montmorillonite. These were deficient in potassium, and so this element must have been added under marine conditions. It has long been known that clay materials tend to fix potassium at the expense of sodium, even when present in low concentration, and it seems probable that this tendency, aided by time and other geologic processes, has tended to change montmorillonite and possibly kaolinite to hydrous micas.

Kaolinite is in general the most stable of all the clay minerals and probably forms under the widest range of conditions. Most kaolinite forms at low temperature, although a very few occurrences are reported to be the result of mineralizing processes in the presence of warm waters. However, where hydrothermal processes are clearly indicated, dickite, another of the kaolin minerals, has commonly formed rather than kaolinite.

Montmorillonite or beidellite, occurring in soils and in bentonites, has formed at low temperatures, but in the hot-spring area of Yellowstone,[31] it has formed in the presence of alkalis at a temperature of at least 205°C. and at pressures of 277 lb. per sq. in. It has also been identified in mineral deposits associated with minerals of hydrothermal origin. Montmorillonite breaks down into other materials and very commonly into kaolinite. This is probably due to the essential role which bases play in its composition, and where these tend to be removed from the system, montmorillonite is not stable. On the other hand, there is evidence that montmorillonite may form over a rather wide range of temperatures, provided other conditions are favorable.

The mode of formation of the various clay minerals and the accessory elements which accompany them affect the quality of these clays and their possible availability for various commercial uses. Kaolinite as a mineral is essentially free from bases and iron, and the quality of a commercial kaolin is dependent on the success in freeing it from accessory materials which will be the ones to carry undesirable elements. In contrast with this, montmorillonite will always carry Ca, Na, or both as base-exchange materials, and it will normally carry Mg as a part of the crystal lattice. The proxying of Al by Fe means that in general it will carry iron. Chemical analyses of large numbers of bentonites indicate that, in general, they will carry 1.5 to 4.0% of Fe_2O_3. A very few bentonites, evidently those formed under exceptional conditions, carry only a few tenths of Fe_2O_3 (see analysis (2), Table I). The low-iron bentonites are all of the calcium type, which have limited dispersibility (colloidal properties), and the sodium types are commonly moderately high in iron and in excess silica present as cristobalite or opaline silica. The magnesian clay, hectorite, is very low in iron and is of the very highly dispersible type with Na as the exchangeable base.

The calcium bentonites may readily be converted to

[30] W. Noll, "Synthese von Montmorilloniten," *Chem. Erde*, **10** [2] 129–54 (1936); *Ceram. Abs.*, **16** [3] 99 (1937).

[31] C. N. Fenner, "Bore-Hole Investigations in Yellowstone Park," *Jour. Geol.*, **44** [2, Part 2], 225–315 (1936); *Chem. Abs.*, **30** [13] 4441 (1936).

sodium bentonites by treatment with a sodium salt when they will have as high colloidal properties as the naturally occurring sodium bentonites. However, removal of excess sodium salts is necessary to prevent flocculation, and this presents certain difficulties.

Members of the hydrous-mica or bravaisite group, which occur most widely in soils, marine shales, and deposits approaching bentonites in purity, are rare. The purest naturally occurring material of this type is probably some of the deposits of Ordovician bentonites, a material different in mineral composition from the normal montmorillonite types of bentonite. An analysis of the clay mineral, bravaisite, from an Ordovician bentonite is given in analysis (2) Table II. The analyses in Table II show that this type of clay mineral is similar to that of montmorillonite in iron and in magnesia content, but it differs in the potassium content.

Studies of pure minerals have had some very practical applications especially to soils. In particular, they have given a clear picture of the way in which crystal structure controls the chemistry of base exchange. The techniques for assuring pure materials have facilitated studies by those interested in some special property of clays or their applicability to special uses. Many avenues of study will no doubt occur to those interested in improving old uses or in finding new uses for clays. Future work, however, will no doubt turn more and more to an understanding of the mixtures which constitute clays, shales, and soils. Thus, the mineralogic studies of pure materials are but the basis for a much broader program of research, one in which mineralogists, geologists, ceramists, and soil specialists must all cooperate. Clays are the most universal of all minerals; they are the basis for all plant growth and hence all life; their uses in industry are numerous, and they are destined to grow in number and importance. So to ceramists and to soil specialists this importance needs no emphasis.

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EFFECT OF GROUND COATS ON REFLECTANCE OF COVER ENAMELS*

By P. C. Stufft and G. H. Spencer-Strong

Abstract

The problem of color variation in white cover-coat enamels has received considerable attention, but variations in color due to base coat have had little or no consideration. An attempt was made to determine the effect of the base coat by comparing color variations in opaque and superopaque enamels applied over blue, white, gray, red, yellow, and green base coats in weights ranging from 10 to 120 gm. per sq. ft.

The resultant finishes were compared visually and with the aid of the Hunter multipurpose reflectometer. Over the entire range studied, the base coat was found to have a marked effect on the color characteristics of the finish coat. This is true particularly in the lower ranges of application including normal production application weights. Base coats that decreased the reflectance of the cover coat in the blue field, were found to give higher apparent opacity than those which maintained a relatively high blue reflectance.

I. Introduction

The problem of colors in the porcelain enamel industry has received an increasing amount of attention in recent years. Past work on the subject has been divided into two fields of endeavor, (1) the study of colors and their effect on enamels and (2) the method of measuring colors and interpreting the results of such measurements.

The average human eye is so sensitive to color differences that the correlation of results obtained by mechanical color measurements with visual observation is a difficult and involved procedure. Investigators have been astonished at the accuracy of entirely unskilled observers, who, almost by intuition, sense minute color variations between samples.

The effect of small color variations in white cover-coat enamels is well known, and a number of papers[1] have been written on their control and measurement.

The effect of the ground coat on the color of the cover-coat enamel has not, however, received a great deal of attention.† The normal commercial ground

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Enamel Division, No. 14). Received March 9, 1945.

[1] (*a*) M. E. Manson, "Some Notes on Color of Antimony Enamels," *Jour. Amer. Ceram. Soc.*, **8** [7] 437–40 (1925).
(*b*) J. L. Michaelson, "Color Measurements," *ibid.*, **20** [3] 67–71 (1937).
(*c*) L. C. Athy, "Tin Oxide Comparison by a General Electric Color Analyzer," *Enamelist*, **9** [10] 17–20 (1932); Enamel Bibliography, 1944 ed., p. 16.
(*d*) L. Vielhaber, "Luster and Opacity of Enamels," *Emailwaren-Ind.*, **12** [22] 177–78 (1935); Enamel Bibliography, 1944 ed., p. 291.
(*e*) "Color Matching Booth," *Steel*, **100**, 64 (May 10, 1937); news note in *Bull. Amer. Ceram. Soc.*, **16** [6] 274 (1937).
(*f*) G. H. McIntyre, "Color Matching of White Parts," *Proc. Porcelain Enamel Inst. Forum, Third Forum, Oct., 1938*, pp. 163–87; Enamel Bibliography, 1944 ed., p. 183.
(*g*) K. P. Azarov and N. S. Kharchenkova, "Determination of Whiteness of Enameled Ware," *Zavodskaya Lab.*, **7**, 238–39 (1938); Enamel Bibliography, 1944 ed., p. 17.
(*h*) "Symposium of Color Standards and Measurements, I–V," *Bull. Amer. Ceram. Soc.*, **20** [11] 375–402 (1941).

† The fact that color of ground coats may affect the color of superimposed cover coats was reported by W. N. Harrison, National Bureau of Standards, to the Committee on Standardization of Tests of the Porcelain Enamel Institute during the preparation of a standard reflectance test for opaque white porcelain enamels in 1937.

coat is basically a very dark blue enamel over which are applied one or more coats of cover-coat enamel for the purpose of hiding the ground coat, giving the article the desired color (usually white), and producing the desired final finish. During the firing operation, the color of the ground coat has been presumed to be constant. Variations in ground-coat color due to over- and under-firing have not been considered.

Colored ground coats have been available for many years. Their chief use, however, has been in the production of specialty items, finished in a single coat, for example, roofing shingles and room heaters, rather than as a base coat for white enamels.

The majority of porcelain enameled ware at the present time, aside from porcelain enameled signs and hollow ware, is finished in white enamel which may cover the entire article or be broken by a strip of black at the edges of the parts. Until the beginning of the war years, the trend in the industry was toward the elimination of the black edging. History, however, has shown that the termination of most major wars results in a great exploitation of the use of colors. This was true at the end of the first world war and that it will follow the present war cannot be doubted; in fact, designers and decorators are already publishing pamphlets and giving lectures to manufacturers on how to make the public color conscious and how to use colors to improve the salability of products. What combinations the postwar designer may call for are at present unknown. Designers, however, have always been interested in color and combinations thereof and there is some indication that the decorative effects obtainable by the use of colored edgings in place of the present black edge may be intriguing to them.

A further development carried on from the prewar period is the enamelers' desire to reduce total enamel thickness. In this respect, an increasing amount of thought has been given to the possibility of eliminating the blue ground coat and the substitution of one or two coats of white enamel applied directly to the iron. There is also continued and increasing interest in producing ware with a single application of white cover-coat enamel over the blue ground coat.

The effect of any or all of these changes on the color of the white enamel coating is a matter of considerable interest and importance to the industry since it may affect either adversely or beneficially the problem of satisfactory color matching of enameled products. Along the same lines, there is the possibility that some of the color differences which have been observed in white cover-coat enamels in the past may be attributable, at least in part, to color variations in the ground coat.

The present paper is concerned with the preliminary investigation of the effects of the color of base coatings on the resultant cover coat.

II. Method of Procedure

For the purpose of making a study, an opaque enamel, having a diffuse reflectance of 68% when milled without opacifier and applied over standard ground coat in two coats of 32½ gm. per sq. ft. each, and a superopaque enamel, having a diffuse reflectance of 79% when milled without opacifier and applied over ground coat in two coats of 30 gm. per sq. ft. each, were milled in accordance with the following formulas:

Mill formulas for cover-coat enamels

	Opaque	Superopaque
Frit	100	100
Clay	7	7
Opacifier	4	1½
Magnesium carbonate	¼	¼
Water	40	40

Fineness, 2% on 200-mesh screen.*

* P.E.I. Tentative Standard Screen Test for Wet-Milled Porcelain Enamel, November, 1938. Porcelain Enamel Institute, Inc., Washington, D. C.

TABLE I

BASE-COAT ENAMEL COLOR CHARACTERISTICS

Base-coat color	Diffuse reflectance (%)		
	Blue	Green	Amber
Red	<8.0	<8.0	15.0
Yellow	<8.0	38.8	45.5
Green	12.6	8.6	<8.0
Gray	13.5	13.0	12.6
White	55.5	54.0	52.0
Blue	<8.0	<8.0	<8.0

The cover-coat enamels were applied over standard blue, white, red, yellow, green, and gray bases, having the color characteristics shown in Table I as measured on the Hunter multipurpose reflectometer.

The blue, white, and gray coats were applied directly to the iron. For simplicity and in order to obtain brighter colors than those normally used with ground coats, the red, yellow, and green enamels were produced from standard clear cover-coat enamels containing the proper coloring oxides and were applied over the standard blue ground coats.

The opaque cover-coat enamel was applied over a range of 10 to 120 gm. per sq. ft., in increments of 10 gm. per sq. ft. up to 80 gm. and in increments of 20 gm. per sq. ft. from 80 to 120 gm. The superopaque enamel was applied in weights ranging from 10 to 100 gm. per sq. ft. in increments of 10 gm. per sq. ft. over a range of 10 to 60 gm. and in increments of 20 gm. per sq. ft. from 60 to 100 gm.

Color measurements were made on the Hunter multipurpose reflectometer, and color properties were computed according to the Robertson and Milligan adaptation of Hunter's chromaticity diagram.[2] The sample plates were also compared visually in order to determine the effect of the color of the base coat on the apparent covering power of the enamel.

III. Results

(1) Visual Examination

Visual examination showed that, except for the gray base coats, the individual base coats maintained their identity over the entire application range. The color properties of both types of enamel applied over the gray base coat were identical with those of the blue

[2] R. M. Robertson and L. H. Milligan, "Symposium on Color Standards and Measurements: IV, Readily Visualized System for Measuring Color of Surfaces," *Bull. Amer. Ceram. Soc.*, **20** [11] 387–91 (1941).

ground coat at application weights of about 50 gm. per sq. ft. with the opaque enamel and about 40 gm. per sq. ft. with the superopaque enamel. At lower application weights, the gray base coat showed more opacity than the blue. With the other specimens, it was possible for even unskilled observers to distinguish between the plaques regardless of the application weight of the cover-coat enamel. For example, a 100-gm. application of superopaque enamel giving an opacity of 85% still showed some individual differences due to the color of the base coat. This phenomenon was even more pronounced with the opaque enamel. In the 120-gm. specimens in this class, it was possible not only to note the differences in the color of the specimens due to the base coat but in several instances to identify the color of the base coat. When specimens showing similar diffuse reflectance as measured with the green filter on the Hunter multipurpose reflectometer were compared visually, the base-coat colors were found to give rise to an illusion of differences in opacity between the specimens; for example, visual observation indicated some specimens to have comparable opacity whereas actually there was a difference of as much as 4% between them when the diffuse reflectance was measured on the Hunter instrument. This illusion was more pronounced at a reflectance of below 80%.

The enamels applied over the red base coat showed the greatest apparent visual opacity followed by the yellow and white base coats. The green base coat, on the other hand, appeared to have less opacity than that indicated by the reflectometer when compared with specimens applied over the normal blue ground coat.

(2) Tristimulus Color Curve Comparison for Opaque Enamel

The results of tristimulus color measurements obtained with the Hunter reflectometer from samples of the opaque enamel applied over the various colors are shown in Figs. 1 to 5. Because the diffuse reflectance approaches saturation with this enamel at an application weight of about 80 gm. per sq. ft., the curves have not been carried above this weight although data were obtained up to 120 gm. per sq. ft. It was believed, however, that the inclusion of the additional data would not be of sufficient value to offset the complications arising from its inclusion because, at these weights, the curves are very close together.

Figure 1 shows a comparison of the tristimulus color characteristics of the opaque cover-coat enamel applied over a standard blue ground coat and over a white base coat. The characteristic color of this enamel at saturation reflectance, in each case, is a cream-white rather than a blue-white; as the saturation point is approached, the No. 2 curve, showing the readings in amber, indicates a greater increase in reflectance than either the blue curve (No. 1) or the green curve (No. 3). The effect of the creamy color characteristic of the enamel is such that the enamel reaches saturation in the blue much earlier than with the other two colors. It is interesting to note that the white base coat gives rise to this saturation at a much lower application weight than the enamel applied over the standard blue ground

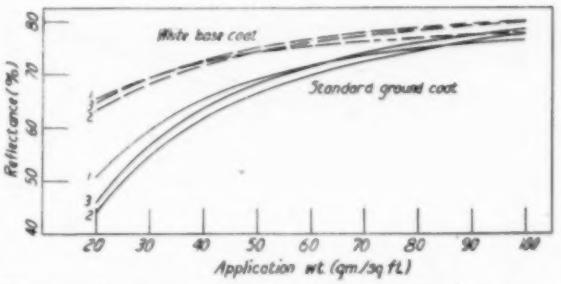

FIG. 1.—Opaque cover coat, blue vs. white base coat: *Curves* (1) blue, (2) amber, and (3) green.

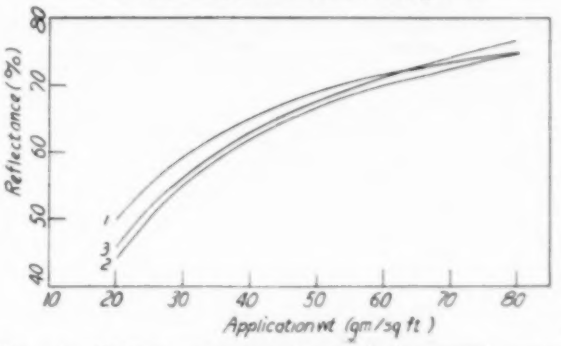

FIG. 2.—Opaque cover coat, standard ground coat: *Curves* (1) blue, (2) amber, and (3) green.

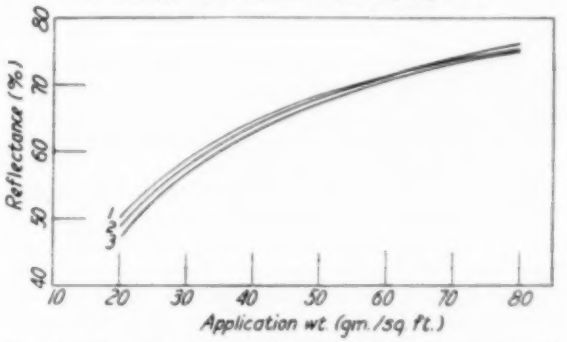

FIG. 3.—Opaque cover coat, red base coat: *Curves* (1) blue, (2) amber, and (3) green

coat. In the white base coat, the blue line (No. 1) crosses the green at 30 gm. application and the amber at 50 gm. With the blue ground coat, the green curve is crossed at about 62 gm. per sq. ft. and the amber at an application weight of about 85 gm. per sq. ft. Thus, the same cover-coat enamel, when applied over the blue base coat, begins to show its cream cast at application weights ranging from 40 to 50 gm., whereas, with the blue ground coat, the creamy cast is not so apparent until application weights of 60 to 80 gm. have been reached. The actual reflectance of the enamels as measured with the green filter show the color change at about 2½% lower reflectance with the white base coat than with the blue ground coat, thereby explaining the pseudoreflectance or increased apparent reflectance obtained when samples of the two specimens with the same measured reflectance are compared.

The opaque enamel applied over the white base coat begins to approach saturation at application weights of

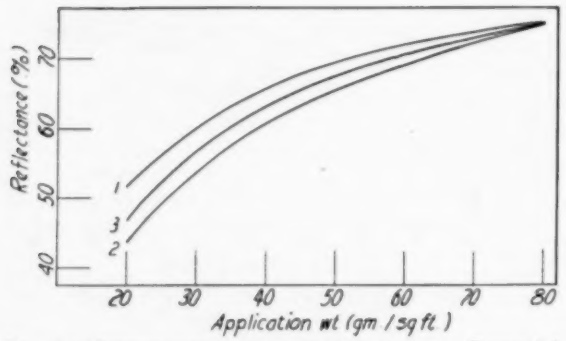

FIG. 4.—Opaque cover coat, green base coat: *Curves* (1) blue, (2) amber, and (3) green.

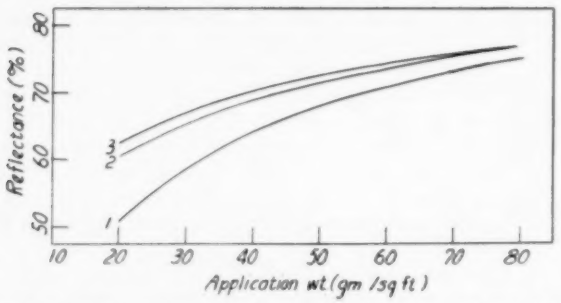

FIG. 5.—Opaque cover coat, yellow base coat: *Curves* (1) blue, (2) amber, and (3) green.

about 60 gm. per sq. ft. or slightly higher, whereas, in the blue ground coat the saturation is approached in the range of 100 gm. per sq. ft. If the curves are carried on, the reflectance of the two enamels in the green will eventually more or less coincide.

Figure 2 shows the color characteristics of the standard blue ground coat, and Fig. 3, the color characteristics of the opaque cover coat over the red base coat. The saturation color characteristics of the enamels applied over the red base coat are approximately the same as those of the blue ground coat. The blue curve is approximately the same with the red as with the blue; the amber curve (No. 2), however, shows a higher reflectance at the lower application weights; and, although the green is approximately the same at the lower application weights, it is lower at the higher application weights.

Although theoretically on the basis of the reflectance curves, the opaque cover coat, as applied over the red base coat, should be more nearly neutral than the same enamel applied over the blue base coat, actually the red tint from the base coat is discernible through the cover coat even at very heavy application weights and in spite of the fact that the blue curve is predominant in the lower portions of the field.

Figure 4 shows the color characteristics of the opaque enamel applied over the green base coat. These characteristics are similar to those of the blue ground coat except that both the blue and green curves are slightly higher than those of the blue ground coat, and the amber curve is slightly lower over most of the range. The curves merge at an application weight of 80 gm. per sq. ft. The effect of this base coat is to overcome the creamy cast in the cover coat by holding down the reflectance of the amber and the net effect is a bluish-green cast enamel which has an apparent visual reflectance lower than that measured by the instrument.

Figure 5 shows the opaque cover coat applied over the yellow base coat. The reflectance of the yellow base coat in both the green and the amber, as shown in Table I, was much higher than with any of the other base coats except the white and, as a result, the initial reflectance at very low application weights is correspondingly higher in the green and the amber. The blue rather closely approximates the blue curve with the blue ground coat. With this enamel, the green and the amber curves merge at an application weight of about 80 gm. per sq. ft. or a reflectance of about 77%. It is indicated that the yellow base coat probably had a slight greenish tinge.

None of the other base coatings gave as much additional reflectance to the cover coat as does the white. In fact, the saturation reflectance in all of the colors, except the white, is approximately the same, although there is some difference in the reflectance measurements with the several colors at this point, indicating the effect of the base coat in spite of the application weights and reflectance involved.

(3) Tristimulus Color Curve Comparison for Superopaque Enamel

Figures 6 to 10 show the tristimulus color curve comparison of the superopaque enamel applied over the various base coats. Figure 6 shows a comparison of the standard blue ground coat and the white base coat; in general, the same effects as noted in Fig. 1 are shown in Fig. 6. Since the color characteristics of the superopaque enamel are somewhat different from those of the opaque cover-coat enamel, there is some variation in the slope of the curves. The blue again predominates in each of the lower application weights and is crossed by the green with the white base coat at an application of 40 gm. per sq. ft. and by the amber at 65 gm. per sq. ft., whereas with the blue ground coat the green curve crosses the blue at 65 gm. per sq. ft. and the amber crosses the blue at about 82 gm. The enamel applied over the white base coat again shows less variation between the tristimulus curves, in fact, the superopaque enamel is more neutral than the opaque enamel.

Figure 7 again shows the reflectance curve for the standard ground coat, and Fig. 8, the superopaque enamel applied over the red base coat. With the superopaque enamel, the curves approached saturation at about 60 gm. per sq. ft. and are plotted at application weights ranging from 20 to 60 gm. per sq. ft. rather than over the entire range.

With the red base coat, the blue curve is practically identical with that of the blue ground coat and the green and amber curves are identical with each other, both being somewhat higher than the similar curves with the blue ground coat.

It is interesting to note that in view of the slight cream cast of the superopaque enamel, the green curve is increased so that it falls exactly on the amber curve rather than below it as was shown on Fig. 3.

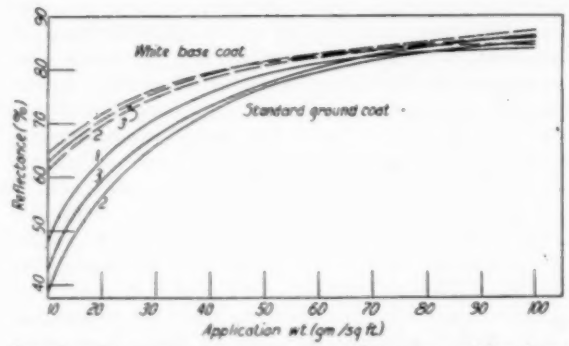

FIG. 6.—Superopaque cover coat, blue vs. white base coat: *Curves* (1) blue, (2) amber, and (3) green.

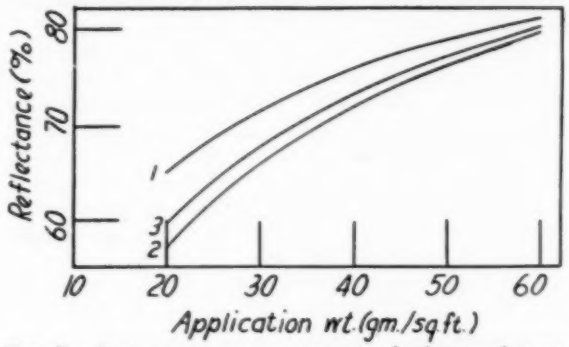

FIG. 7.—Superopaque cover coat, standard ground coat: *Curves* (1) blue, (2) amber, and (3) green.

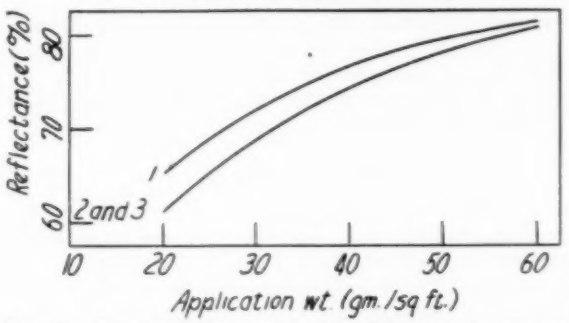

FIG. 8.—Superopaque cover coat, red base coat: *Curves* (1) blue, (2) amber, and (3) green.

The tristimulus reflectance curve of the superopaque enamel applied over the green base coat of Fig. 9 shows results similar to those of the opaque enamel, that is, the reflectance in all three colors is increased.

Figure 10 shows the effect of a yellow base coat. The blue curve falls exactly on the same curve for the blue ground coat with the amber and the green curves lying above it. The color of the cover coat again is sufficient to increase the reflectance in the green.

The superopaque enamel applied over the yellow base coat shows much less difference in color than when the opaque cover coat was applied over the same base coat and a much greater tendency toward a neutral shade as the saturation point is approached.

The results obtained with the superopaque enamel, in general, were similar to those of the opaque enamel, except that the increased opacity of the superopaque

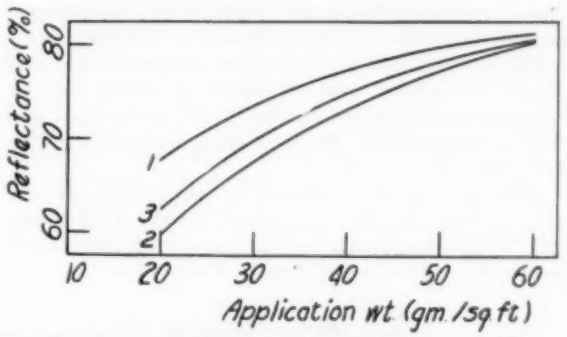

FIG. 9.—Superopaque cover coat, green base coat: *Curves*, (1) blue, (2) amber, and (3) green.

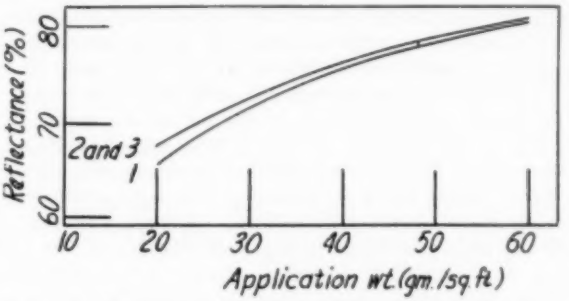

FIG. 10.—Superopaque cover coat, yellow base coat: *Curves* (1) blue, (2) amber, and (3) green.

enamel decreased the color variation in degree. Even with the superopaque enamel reaching opacities considerably in excess of 80%, the color characteristics of the base coat are still carried over into the cover coat.

IV. Application of Results to Chromaticity Diagram

It was believed that the application of these color data to the revised Hunter chromaticity diagram might be of interest, especially a comparison of visual results with those of the diagram. In order to make a comparison, the chromaticity data were calculated for the opaque enamel over the several base coats at application weights sufficient to give 60 and 80% reflectance when measured with the green filter on the Hunter instrument and with the superopaque enamel at reflectances of 65 and 80%.

The results of these computations, unfortunately, were at such variance with the visual observation and even with the tristimulus color curves that they are believed to be undependable and therefore have not been included in the data. For example, the opaque white enamel sample, showing a reflectance of 60% when applied over the white base coat, actually had a cream tint and, therefore, would have been expected to fall in the yellow-green field; actually, it was found to fall in the blue-green field, showing a higher blue value than the blue ground coat. Similarly, the red, which showed a definite red color at 60% reflectance, was found to fall in the blue-purple field. The 80% reflectance results with the green, white, and blue were identical on the diagram although entirely unskilled observers were able to classify the resultant sample

plates without difficulty. With the superopaque enamel (according to Fig. 8), the green specimen showing 65% reflectance also fell in the red-purple field and should have been twice as strong a red as the red sample with the opaque enamel at 60% reflectance and was far more red than the same enamel applied over the red base coat.

Although this system may be satisfactory for the classification of widely dissimilar colors, it obviously fails when attempting to compare minute differences in color as caused by the effect of a base coat.

V. Enamel Thickness

In view of the fact that the white base coat gave the largest increase in reflectance, comparative data were obtained on the reflectance and coating thickness with the Hunter green filter for both the opaque and superopaque enamels over the blue and white base coats.

With the opaque enamel, an additional thickness of three mils was required to secure the same reflectance with the blue ground coat as that obtained with the white base coat in the range of normal commercial enamel applications. Similarly, $1^1/_8$ mils additional application was required with the superopaque enamel on the blue base coat. Since these measurements do not take into consideration the pseudo-opacifying properties of the enamel applied over the white base coat due to color variation, they represent a minimum thickness of color variation required to produce comparable results. In the moderate weights in commercial use, the apparent increase in opacity due to color variation adds the equivalent of 2% or more reflectance to the enamel applied over the white base coat so that to obtain any actual semblance of a comparative match between the coatings an even greater application over the blue base coat would be required.

VI. Discussion of Results

The foregoing data indicate that the color of the base coat has a pronounced effect on the color and apparent reflectance of white cover-coat enamels; in fact, these effects were much more pronounced and persistent than had been anticipated. It is indicated, therefore, if designers attempt to dictate the use of a red- or yellow-edging material in place of the conventional black, that the white enamel adjacent the edging material may be expected to show different color characteristics than the rest of the panel. Should it be desired to have edges of more than one color on the same article, even wider variations in apparent reflectance and color may be expected. Similarly, the use of ground coats of varying color in the same plant with the same cover-coat enamel application may be expected to give rise to some difference in the color of the final white cover-coat enamel.

The results of the final observations indicate that the human eye is more sensitive to color variations than the reflectometer. It has long been contended that only an exceptional and experienced operator can discern differences of as little as $1^1/_2$% reflectance as measured on the reflectometer and it is practically impossible to discern differences of less than 1%. In the present investigation, however, instances were noted where variations between the actual measurements made on the reflectometer of approximately 1% or less were readily detected by entirely unskilled observers.

The study also indicates clearly the effect of minute color differences on the apparent whiteness or opacity of enamels as judged by the observer; thus, cover-coat enamels applied over a white base coat were judged by visual observers to possess 2 to 3% more reflectance than enamels applied over blue or green base coats having the same measured diffuse reflectance, and the variation was even more pronounced with the red and yellow base coats.

These deviations between the measured and observed reflectances were not predictable on the basis of the chromaticity data. The chromaticity diagram shows the opaque cover coat applied over the white, green, and yellow base coats, and all at 80% reflectance in the green, to be very nearly the same color, whereas the visual observer noted considerable variation in the color. The deviation between the enamels, shown in the chromaticity diagram, is not great except possibly the yellow at 60% reflectance, whereas the visual comparison showed a considerable difference between the color of the several enameled specimens.

Color trends in the white cover-coat enamels probably may be predicted better on the basis of the tristimulus reflectance curves than on that of the chromaticity diagram. The amount of variation between the observed and measured results again indicates the desirability of a more satisfactory method than is now available for color determinations and comparisons.

VII. Conclusions

(1) The color of the base coat underlying opaque enamels affects that of the cover-coat enamel at application weights extending over the range of 10 to 120 gm. per sq. ft. and with reflectances up to 80%.

(2) The color of the base coat underlying superopaque enamels affects the color of the cover coat at application weights of 10 to 100 gm. per sq. ft.

(3) Variations in cover-coat colors are greatest at lower application weights, and they decrease as the cover-coat application weight and opacity increases.

(4) Certain base-coat colors, especially red, yellow, and white, have a tendency to produce color variations in the cover-coat enamel which give rise to visual reflectance greater than the actual reflectance of the enamel as measured on the reflectometer.

(5) Base-coat color variations are believed to be more important than has been assumed previously and may have been partly responsible for some of the color-matching problems in the enamel industry.

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Baltimore 24, Maryland

STRAINS IN GLASS PRODUCED BY APPLIED COLOR LABELS*

By J. E. Ablard

Abstract

The fact that "applied color lettering" can weaken a bottle has been recognized from the beginning of the practice, and the fact that it normally does not but may even increase the strength slightly is also well known. Weakness arising from the "color" causes fractures with origins on the outer surface of the bottle wall and within the colored area. They are thus readily distinguished from those fractures which arise from weaknesses of the inside surface of the wall.

The author investigated this subject with commercial and experimental colors on pressure bottles of various manufacturers. A special thermal-shock test was used, which tests the strength of the barrel of the bottle without producing large strains on the base. By correlation of such shock tests with the strain patterns observed in ring sections examined under the polarizing microscope and with thermal-expansion data, it has been possible to set up a suitable procedure for insuring the proper "fit" of a ceramic color to a glass. With minor exceptions, the problem is considered to be similar to those of applying enamels to metals, glazes to pottery, and in sealing metals to glass, which have already been discussed in the literature.

By an analysis of the respective thermal-expansion curves for the glass and the ceramic colors, the author suggests the reason for the experimentally found fact that the ceramic color must be of slightly lower coefficient of expansion than the glass in order to minimize the strain between the color and the glass when the color has been fired on to the glass and the two cooled down to room temperature. The suggested reason is that the fluxes used in the manufacture of ceramic colors are of necessity softer than the glass and, therefore, their annealing range is below that of the glass. From the shapes of the respective total expansion curves, it is shown that, when the color passes through its lower critical annealing temperature, its curve falls below that of the glass. If the coefficient of expansion for the color is less than that of the glass, the lower rate of contraction of the color balances out this initial high contraction so that at room temperature no residual strain is left.

A brief discussion of the interface between the glass and the ceramic color is also included, with particular reference to the case of a flux containing lithia. The small-diameter, highly mobile lithium ion migrates into the glass, creating an interface tension cord, visible under the polarizing microscope. Present information shows that this is permissible, provided the other factors mentioned have been properly adjusted.

I. Introduction

Vitrifiable glass colors or enamels have been used for many years, primarily for decorative purposes. Since 1934, new uses have necessitated increased chemical resistance in these enamels. Colors to be used for the labeling of milk and beverage bottles must be resistant to the action of the alkali used in the washing compounds. Enamels used in over-all sprayed glassware must, for the sake of health, be resistant to weak acids. Glass colors are composed of a "flux" or "glaze" into which has been ground a suitable inorganic "pigment" or "oxide." When the color is fired on to the glass, the pigment remains essentially unchanged, but the flux melts, flows down on the glass, and fuses to the glass surface. During the annealing period there is a gradual transition to the hard, glassy state; in fact, the glass color forms a glassy layer on the surface of the glass on which it has been applied.

The glazes used in low-fire colors of the earlier era were in general low-melting, lead borosilicate glasses. Colors made from them had practically no chemical resistance. The present-day resistant colors are made from glazes composed of six or more glassmaking oxides. The correct thermal expansion, melting temperatures, and resistant qualities have been more difficult to attain and control in the complex composition. Later in the nineteen thirties, colors of greater alkali resistance were produced for labeling milk and beverage bottles to meet the more stringent specifications relating to alkali resistance which the bottle manufacturers had developed. Soon after that, however, some of the glass manufacturers began the production of bottles from an improved, stronger glass, which had a lower coefficient of expansion than the glasses previously used. There was some breakage reported in bottles on which vitrifiable color labels had been applied. The present study was initiated in 1939 in order to determine the cause of this breakage so that it could be eliminated.

II. Preliminary Experimental Investigations

(1) Effect of Applied Color Labels on Thermal-Shock Strength

Since a fracture diagnosis of the isolated instances of

* Presented as supplementary title at the Forty-Fourth Annual Meeting, The American Ceramic Society, Cincinnati, Ohio, April, 1942 (Glass Division). Received April 9, 1945.

TABLE I

THERMAL-SHOCK TESTS ON DECORATED VERSUS UNDECORATED BOTTLES

Glass manufacturer No. 1			Glass manufacturer No. 2		
	Cumulative breakage (%)			Cumulative breakage (%)	
Differential (°F.) (1)	Decorated* (2)	Plain† (3)	Differential (°F.) (4)	Decorated* (5)	Plain† (6)
Special side-wall thermal-shock test; bottles inverted, bases cool					
60	5		100	4	0
75	75		110	5	0
80	100		115	9	0
100		50	120	9	0
105		100	125	13	0
			130	14	4
			135	32	9
Orthodox thermal-shock test (heel test)					
75	No test	50			
85	" "	100			

* Fracture origin chiefly "under the color."
† Fracture origin chiefly in bruises in shoulder and upper side wall.

breakage in service indicated that certain applied color labels imparted a low thermal-shock strength to the bottles, the thermal-shock test was selected as the most promising laboratory test method for comparing the mechanical strength of "decorated" and "undecorated" bottles. A modification of the orthodox thermal-shock test[1] is necessary, however, since the orthodox test is essentially a test of the heel of a bottle; the heel is more severely stressed by this test than the side wall on which the label is usually fired. In the modified test, therefore, the heel was eliminated from the test by inverting the bottles in the basket and lowering the hot-water level or by adjusting the height of the rack so that only the necks and side walls to within 2 in. of the bottoms of the bottles were immersed in the hot water. Thus the bases of the bottles were kept relatively cool as compared with the label area and were subjected to a relatively mild shock. This modified test is known in the glass container industry as the side-wall thermal-shock test.

Plain bottles were obtained from two different manufacturers. One half of each lot was decorated with a fusible color that had a coefficient of thermal expansion greater than that of the bottle glass and was therefore apt to decrease the mechanical strength of the bottles. The other half was used for controls and remained undecorated. The undecorated bottles from manufacturer No. 2 were handled so as to make them true controls, that is, they were run through the decorating lehr immediately following the decorated bottles, and care was taken in handling to make sure that the bruising on the surfaces was no greater than that on the decorated bottles. All four lots were given the side-wall thermal-shock test at an appropriate differential, and the test was then repeated at progressively higher differentials until considerable breakage accumulated. In addition, the orthodox thermal-shock test at 75° and 85°F. differentials was given to undecorated bottles from manufacturer No. 1. For all bottles broken in the test, the origin of the fracture was determined. Most origins in the decorated bottles were in the decorated region, that is, under the color, and those on the plain bottles were in bruises in the shoulder or upper side wall and in the heel.

The data are given in Table I. Comparison of the data in columns (2) and (3) and also in (5) and (6) shows clearly that this particular fusible color reduced the strength of both lots of bottles, and the existence of origins "under the color" in the decorated bottles supports the conclusion that the fusible color affects the strength.* Comparison of the top and bottom sections of the left side of Table I shows that the side-wall test is 20° to 25°F. (differential) less severe than the orthodox heel test or rather that the side-wall strength of a bottle normally is 20° to 25°F. greater than the heel strength.

(2) Relations Between Thermal Expansion, Polariscopic Strain Pattern, and Thermal-Shock Strength

The relations between (1) the coefficient of thermal expansion of the fusible color and glass, (2) the strain pattern observed in the glass by means of the polarizing microscope,[2] and (3) the thermal-shock strength were next investigated. A series of fluxes containing lead oxide, boron oxide, silica, and sodium oxide in varying amounts were melted down, fritted, and ground with 5% TiO_2 to make experimental white colors of different coefficients of expansion. The compositions appear in the top section of Table II. The coefficients of expansion of the fluxes used to make the colors are presented below, together with that of the glass from bottles on which the colors were applied. When ring sections were cut from the decorated bottles and examined under the polarizing microscope, the strain patterns which appeared directly under the ceramic color on the ring section were observed and the optical-path difference was measured. Thermal-shock tests as described previously were performed on lots of fifty bottles of each of the colors.

These data appear at the bottom of Table II. The

[1] Standard Method of Thermal-Shock Test on Glass Containers, A.S.T.M. Designation C149–43, 1943 Supplement (Part II) to A.S.T.M. Standards, pp. 37–39. American Society for Testing Materials, Philadelphia 2, Pa.

* To appreciate the reason for a thin layer of one glass having such a marked effect on the strength of a much thicker one, it should be remembered that if the two glasses contract at different rates one will be stretched and the other compressed. Since the thicker layer is more rigid, the thinner layer will undergo more distortion in order that the stresses be balanced. A small strain in the bottle wall produced by the applied color is therefore indicative of a larger strain in the color itself. With this in mind, it is easily understood why the color might give way, and, from the pattern of the breaks observed, it appears that once a crack is started it propagates into the glass. Decorated bottles containing tiny surface cracks in the color label are described as "crazed," a term borrowed from much the same type of phenomenon sometimes observed in pottery and porcelain enamel manufacture. Thus fractures arising from tension in the color label originate on the outside surface of the wall and are readily distinguished from those due to weaknesses of the inside surface of the wall.

[2] Glass Container Association Standard Testing Procedure Subcommittee, "Polariscopic Examination of Glass Container Sections," *Jour. Amer. Ceram. Soc.*, **27** [3] 85–89 (1944).

TABLE II

COMPARISON OF COEFFICIENT OF EXPANSION, POLARISCOPIC STRAIN, AND THERMAL-SHOCK STRENGTH

	Flux No. 1	Flux No. 2	Flux No. 3	Undecorated (bottle) glass
Composition				
PbO	50.0	51.3	50.9	
SiO_2	35.2	35.7	35.6	
B_2O_3	10.8	9.8	9.9	
Na_2O	3.2	3.2	3.3	
Coefficient of thermal expansion ($\times 10^7$)	69	73	77	87
Optical path difference (strain, mμ/in.)*	+35	−9	−165	
Thermal-shock strength†				
(*a*) Initial breakage level	145	105	80	135
(*b*) 10% breakage level	165	107	86	145

* Strain in glass observed in ring section of bottle after firing onto glass (bottle), described in the last column, a fusible color prepared from the respective flux; positive sign denotes tension in the glass and compression in the color.

† Side-wall thermal-shock test differential in °F. for fired bottles.

breakage-level data refer to the differential in temperature between the hot and cold baths required to cause (*a*) the first bottle out of fifty to break and (*b*) 10% of the bottles to break. A positive optical-path difference denotes tension; a negative difference, compression.*

Comparison of the results shows that, with increased coefficient of expansion of the flux, the ceramic colors produced strains in the glass under the color varying from a tension in the first case to a slight compression in the second and to a considerably higher compression in the third. An opposite stress, that is, tension, presumably would be in the color. This regular change in strain pattern is accompanied by a decrease in the strength of the bottles. Whereas bottles decorated with a ceramic color made from the first flux appeared to be even stronger than the undecorated bottles, this strength decreased rapidly with increased coefficient of expansion of the flux until the bottles decorated with the same white color made from the third flux were considerably weaker than the undecorated bottles. In the latter case, the bottles would not be acceptable as internal-pressure bottles in the trade.

(3) Relation Between Thermal-Shock Strength and Internal-Pressure Strength

It may be argued that it is needless to worry about the strength of the barrel of the bottle if it is stronger than the base anyway. Usually such high thermal shocks are not encountered in daily use. But it is desirable that the side wall of the decorated bottle be as strong as it was before it was decorated no matter what the magnitude of its strength may be. Furthermore, any decrease in the strength of the side wall would lessen the ability of the bottle to withstand internal pressure. Rather than use the internal-pressure test in the investigation of this problem, which would require considerably more time for large lots of bottles, the inverted thermal-shock test was chosen in which sixty-four bottles could be tested at a time. The comparison between the strength of the bottles as observed in the two tests appears in Table III.

* To convert the optical path difference in millimicrons per inch to stress in pounds per square inch, multiply by 2.2 (see formula (1), p. 87, footnote reference 2.

TABLE III

THERMAL-SHOCK TESTS VERSUS PRESSURE TESTS*

	Initial breakage level	
	Thermal-shock test (°F.)	Sustained pressure test (p.s.i.)
Plain bottles	115	300
Bottles decorated with		
Red in flux A	140	500
White in flux A	125	550
Red in flux B	125	450
White in flux B	120	600

* Standard Method of Hydrostatic Pressure Test on Glass Containers, A.S.T.M. Designation, C147–43, 1943 Supplement (Part II) to A.S.T.M. Standards, pp. 30–33. American Society for Testing Materials, Philadelphia 2, Pa.

III. Control of Strain in Applied Color Labels

(1) Applicability of Polariscopic Ring-Section Method

To measure the coefficients of expansion of all of the glasses on which ceramic colors are applied would be a long and tedious task. Furthermore, it is evident from the data in Table II that, to obtain strong bottles, it is unnecessary to match the coefficients of expansion of the flux and the glass but a flux should be used whose expansion is somewhat lower than that of the glass. To answer the question of how much lower, this series of experiments would have to be carried out on each glass to which the color was to be applied.

Table II suggests that the suitability of a color for application to any glass can be rapidly determined by observing the strain pattern disclosed by the polarizing microscope in a ring section cut from a sample bottle which has been decorated and fired in the usual way. This method has tremendous advantages over the actual expansion measurements and the thermal-shock determinations, not the least of which are the speed with which the work can be done and the availability of the apparatus for making the tests. Most glass manufacturers now have some form of polarizing microscope for inspection of the quality of their regular ware.

After a considerable number of commercial colors had been examined by the ring-section method and comparisons made with the thermal-shock strengths of the decorated ware, the ring-section method of testing was adopted. Many of the glass companies who decorate their ware have also used it. To the knowledge of the writer, no case of breakage due to the application of ceramic colors has been reported when the ring-section samples from the bottles showed either no strain or a tension strain due to the application of the color. It has also been possible to confirm the fact that decorated bottles whose sample ring sections show a slight tension in the glass due to the color will, in general, be stronger than bottles which are undecorated

but have had the same heat-treatment subsequent to their manufacture.

(2) Examples of Polariscopic Strain Patterns

A collection of ring sections of bottles decorated with various colors was acquired, and colored photographs were made of typical cases (see color plate, Figs. 1 to 6). Each photograph was taken through the polarizing microscope with the first-order red tint plate in place. The specimens were oriented in those quadrants in which a blue or green color represents a tension strain in the glass and an orange or yellow color represents a compression strain. The magnitudes of the strains may be estimated from the polariscopic colors.[3] For this examination, the rings were slit lengthwise to relieve any annealing strain.

The dark line at the top of each photograph is the opaque ceramic color on the outside of the ring section. Most of the photographs show distinctly the inside edge of the ring section, which gives an idea of the magnification (about 4.5 times). In Fig. 1, only the neutral pink tint is observed, which is indicative of no strain in the glass resulting from the application of the ceramic color. This ceramic color contains no lithia and has a thermal expansion which matches that of the glass.

In Fig. 2, however, a blue patch just under the ceramic color signifies that the glass is in tension there and the label, therefore, under compression. Several characteristics of such a strain pattern make it certain that the strain is a result of the application of the ceramic color: (1) It appears only under the color; (2) the edges of the blue patch fade into the neutral pink without any clear demarcation line such as is evidenced in the strain patterns of cordy glass; (3) on the inside surface of the ring section, a corresponding yellow color is barely visible, which signifies that the glass there is under compression; this effect would be expected in a slit ring with a compression force on the outside tending to close the slit in the ring; and (4) the external ceramic coat may be removed by a mixture of warm sulfuric and hydrofluoric acids without removing an appreciable amount of glass; when the ceramic color is thus removed, the strain in the glass disappears.

Since the glass under the ceramic color is in tension, the ceramic color itself must be in compression. The compression is the result of less contraction of the ceramic color than of the glass on cooling, that is, the ceramic color has a lower total thermal expansion than the glass. The yellow color in Fig. 3 which appears under the ceramic label is evidence of a compression strain. This is the opposite case; the ceramic color here has a total thermal expansion higher than that of the glass. Such a compression strain pattern, in the light of the data in Table II, is associated with weak bottles and is a warning to the manufacturer that such a color is unsuitable for that particular glass.

IV. Discussion of Fluxes Containing Lithia

Inspection of the photographs of strains in glasses decorated with ceramic colors containing lithia discloses a thin line of blue or blue-green immediately under the ceramic color. Figures 4, 5, 6 are examples of the strains observed under ceramic colors whose total thermal expansions match that of the glass, are less than that of the glass, and are greater than that of the glass, respectively. The sharp blue line is always present in ceramic colors containing lithia, regardless of the relative expansion of the glass and the ceramic color. Removal of the ceramic label with sulfuric and hydrofluoric acids removes the large diffuse patches of blue or yellow color seen under the polarizing microscope but does not remove the sharp, thin blue band near the surface.

Measurements of path differences have been obtained as high as 130 mμ per in. at the edges of a "lithia" blue streak next to the applied color. Unfortunately, the polarizing microscope does not differentiate between birefringence owing to strains and birefringence caused by a quasi-crystalline structure which might be set up on the surface due to lithium-ion migration, so that it is uncertain whether or not the blue streak is truly evidence of strain. It has been noted elsewhere[4] that lithium ions migrate into glass very easily and that this migration produces a decrease in strength of glasses decorated with enamels containing lithia. This defect was claimed to be observed even if the expansion coefficients of glass and enamel are perfectly matched. From the data of Table II, it is apparent that if an enamel were applied to glass of the same coefficient of expansion, it would cause a decrease in the strength of the glass whether it contained lithia or not. On the contrary, experiments show that lithia colors do not decrease the strength of bottles if their *total* thermal expansion is equal to or lower than the glass; in fact, the decorated bottles show as good or better thermal-shock strength than similar undecorated bottles. Table IV shows several different ceramic colors made from fluxes containing lithia in concentrations up to 2% Li_2O

TABLE IV

THERMAL-SHOCK STRENGTH OF COLORS CONTAINING LITHIA

Color and glass No.	Differential for initial breakage (°F.)		Strength increase over undecorated bottles (°F.)	Li_2O content of flux (%)
	Plain	Decorated		
White on No. I	115	125	+10	1.12
White on No. II	95	110	+15	1.12
Yellow on No. III	95	100	+5	1.12
Blue on No. IV	100	105	+5	0.99
Same yellow on No. V	115	130	+15	1.12
White (No. P46) on No. VI	135	165	+30	1
White (No. P25) on No. VI	135	150	+15	2
White (No. P49) on No. VI	135	150	+15	0.5

[3] See Table I, p. 87, of reference 2 or A. J. Monack and E. E. Beeton, "Analysis of Strains and Stress in Glass, I–IV, *Glass Ind.*, **20** [4] 127–32; [5] 185–91; [6] 223–28; (7) 257–62 (1959); *Ceram. Abs.*, **20** [3] 64 (1941).

[4] (*a*) N. J. Kreidl, "Fluxing Properties of Lithia," *Foote-Prints*, **14** [1] 1–11 (1941); *Ceram. Abs.*, **20** [11] 273 (1941).

(*b*) N. J. Kreidl, B. F. Trumm, and R. F. Scott, "Electrolytic Replacement of Sodium by Ammonium in Glass," *Jour. Amer. Ceram. Soc.*, **24** [7] 225–28 (1941).

Fig. 1 Non-lithia containing color—color's thermal expansion matches that of the glass.

Fig. 4 Lithia containing color—color's thermal expansion matches that of the glass.

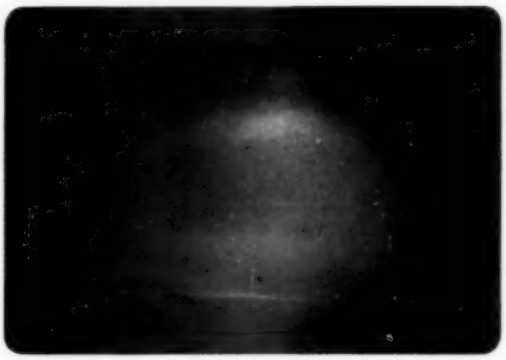

Fig. 2 Non-lithia containing color—color has lower thermal expansion than glass.

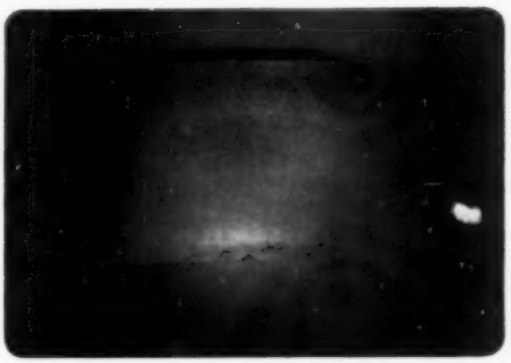

Fig. 5 Lithia containing color—color has lower thermal expansion than glass.

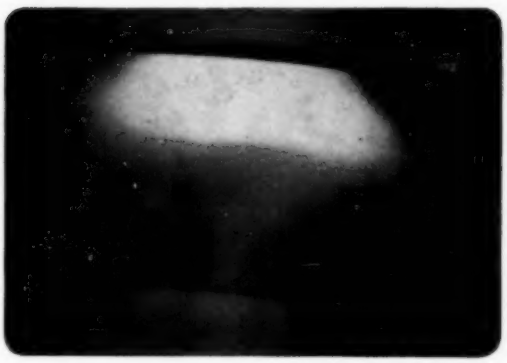

Fig. 3 Non-lithia color—color has higher thermal expansion than glass.

Fig. 6 Lithia containing color—color has higher thermal expansion than glass.

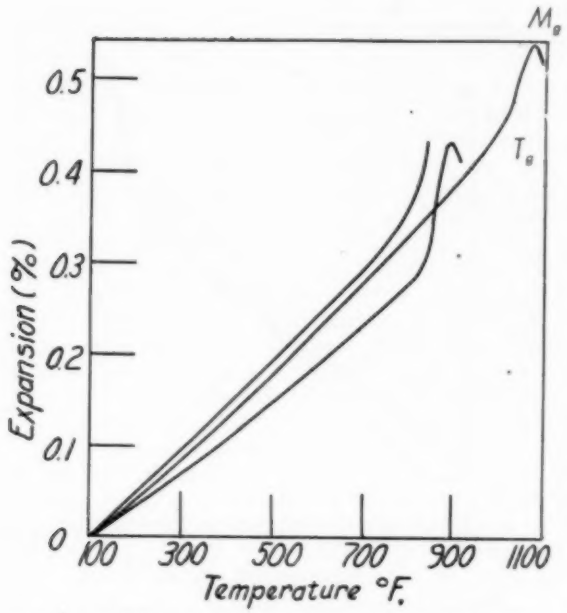

FIG. 7.—Relative expansion of glass and ceramic color.

which were applied to bottles made by six different glass manufacturers. The temperature differentials for initial breakage refer to the failure of the first bottle out of each lot of fifty. The decorated bottles in every case did not break when subjected to thermal shocks which caused the first undecorated bottle to break, and it was necessary to use a differential 5° to 30°F. higher to break the first bottle of those decorated. As in all of these tests, the plain bottles had been sent through the decorating lehr along with the decorated bottles in order to secure the same degree of annealing.

Because of its great fluxing action, lithia is a highly desirable ingredient of acid- and alkali-resisting ceramic colors. From the foregoing information, it became apparent that the lithia diffusion into the glass surface causes no trouble if certain other conditions are met. Fluxes made with lithia must be carefully compounded and controlled in production, else they will show greater tendency to devitrify. Excessive devitrification during the firing cycle can effect a marked change in the properties of a flux. In particular, it has actually been demonstrated that devitrification caused an increase in the coefficient of thermal expansion of one flux from 77×10^{-7} to 142×10^{-7} in. per in. per °F. Of course, if such changes took place on the bottle during the firing cycle, the strength of such decorated bottles would be considerably decreased. A simple test of this tendency to crystallize can be made by observing the change in strength of the bottles with repeated cycling through the decorating lehr. A bottle decorated with a relatively nondevitrifiable color should show no change in strength at the end of the second cycle and may stand three or four cycles without becoming appreciably weakened. A bottle decorated with a ceramic color whose flux has a tendency to devitrify will show a considerable decrease in strength after the second cycle. Some have been known to break in the lehr on the third cycle.

To apply the method of microscopic examination of ring sections for predicting the suitability of a ceramic color containing lithia for application to a glass object, the thin blue or blue-green streak immediately under the color is ignored and observations are made on what polarizing colors are present in much broader, more diffuse bands deeper in the glass. The same rules as those set forth above for nonlithia ceramic colors may be applied to these diffuse bands to predict what effect the lithia-containing ceramic colors will have on the strength of the bottles to which they are applied. Lithia-containing colors which produce strain patterns, such as that in Fig. 5, have been in use for three years or more without any reports of breakage from ceramic label applications.

It should be noted that it is unnecessary to know whether or not the ceramic color contains lithia in order to make this prediction as to the strength of the decorated bottle, so that any decorator has at his disposal the means for control of the quality of his decorated ware, provided only that he has access to a polarizing microscope and the means for cutting ring sections for samples.

V. Importance of Total Expansion in Fitting Ceramic Colors to Glass

The search for an explanation of the need for lower thermal coefficients of expansion for the applied color label than for the glass on which it was to be used led to the conclusion that the factors involved were not the coefficient of expansion as ordinarily determined but the total contractions of the ceramic color and the glass itself when cooled from the firing temperature in the decorating lehr down to room temperature. The differences between the observed total contractions and those which would be calculated from the coefficients of expansion as ordinarily reported are due to certain changes which take place on cooling or heating all glasses. Though not understood in full detail, descriptions of these changes appear throughout the literature and are summarized by Morey.[5]

Figure 7 shows the thermal expansion of a glass and two fluxes plotted against temperature. The longest curve represents the data for the glass. According to the terminology used by Morey, the maxima appearing in the curves are known as the upper annealing temperature, labeled M_g, for the glass. The temperature at which a more or less abrupt change in slope of the curve takes place is known as the lower critical point or transformation point. This would be about 1000°F. for the glass whose expansion is illustrated in Fig. 7 and this point is labeled T_g. The lower critical points for the fluxes are somewhat lower, about 800° and 830°F. The slope of a particular curve from 100°F. to the lower critical point is approximately constant, that is, the curve is approximately a straight line. It

[5] G. W. Morey, Properties of Glass, p. 267. Amer. Chem. Soc. Monograph Series, Reinhold Publishing Corp., New York, 1938. 561 pp.; *Ceram. Abs.*, **18** [2] 48–49 (1939).

has been customary to call the slope of the curve through this range the "coefficient of expansion." The coefficient of expansion is more accurately defined mathematically as $\frac{1}{l}\frac{dl}{dt}$, where l is the length of the specimen under examination at a particular temperature. These curves allow computation of the approximate coefficients of expansions of the glass and of the fluxes. Since the pigment added to the flux to make a ceramic color has only a minor effect on the coefficient of expansion of the finished color, the two flux curves may be considered as representing the expansion of two ceramic colors.

At temperatures corresponding to M_g, the glass would certainly be relieved of any strains existing in it from any previous heat-treatment. But as the glass cools from this temperature down to the lower critical point, it becomes more and more viscous until strains are only relieved with great difficulty below the lower critical point. This will be assumed to be true of the ceramic colors except that the changes take place at lower temperatures, as shown by the curves. (The maximum was not determined for the flux having the higher coefficient of expansion, but it assuredly exists.) The ceramic colors, then, are relatively soft at a temperature of about 200°F. below that at which the glass softens. Actual firing temperatures in decorating lehrs are hard to determine accurately. Thermocouples register about 1200°F., depending on how they are placed with respect to the bottles, but the time in the firing chamber is too short for the glass to become heated to this temperature throughout. The actual temperature experienced by the surface of the bottle and the ceramic color is probably 1120° to 1180°F.

If the two ceramic colors are (separately) applied to a bottle, it will be possible to predict that the bottle made from the glass whose expansion appears in Fig. 7 would be practically strain free (from all thermal causes) when it leaves the firing box. As the bottle travels through the annealing zone, it cools gradually. When the temperature has decreased to about 900°F., the ceramic colors are still quite fluid; however, with further cooling they become nonstrain-relieving solids at around 800°F. The glass, on cooling, contracts according to the curve in Fig. 7. The ceramic color would also contract according to its particular curve except that it is now attached to the bottle and must therefore accept its dimensions. To do so, the ceramic color either stretches or is compressed. The glass itself undergoes the opposite changes to a smaller but none the less important extent. The ceramic color will be stretched if it contracts more per degree drop in temperature than does the glass. It will be compressed if it contracts less per degree drop in temperature than does the glass. In the range between 800° and 900°F., the former is the case so that a tension develops in the ceramic color. This tension in this range would be relieved if the temperature decreased slowly enough, but the length of time required to relieve it increases rapidly as the ceramic color becomes more viscous. In a practical decorating lehr, the bottle moves through the range of 900° to 800°F. in about twenty minutes

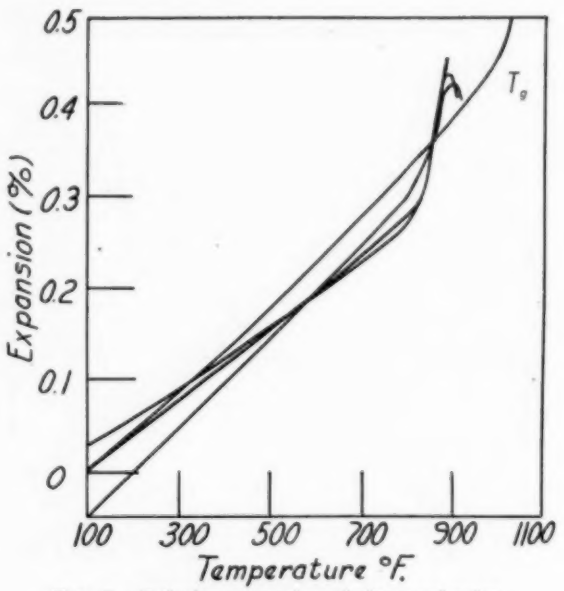

FIG. 8.—Relative expansion of glass and color.

so that some of this tension caused by the rapid contraction of the ceramic color through this range is frozen.

From about 800°F. down to room temperature, the bottle continues to contract and the tension increases or decreases, depending on whether the subsequent contraction of the glass is less than that of the ceramic color or greater. In fact, if the ceramic color contracts sufficiently slowly (the relative contraction per degree Fahrenheit is now essentially constant and numerically equal to the coefficient of expansion as ordinarily quoted), the tension in the ceramic color decreases to zero and may even change to a compression. The opposite strains are experienced by the glass. Thus the glass is usually in a state of compression below about 800°F., but this compression may increase, decrease to zero, or change to tension, depending on the relative magnitudes of the coefficients of expansion of glass and color.

This condition may be represented more clearly by a system of curves such as appear in Fig. 8. The expansion curve for the glass is determined first and then a flux is chosen which, when made into a ceramic color, fired on to the glass, and cooled down to room temperature, produces no strain in the glass under the color at room temperature (or 100°F.). The two curves should cross at room temperature. If one curve is superimposed on the other (vertical displacement without rotation) so that they intersect at 100°F., then the two curves will again cross at some temperature within the annealing range for the flux. This point may be called the temperature at which strains caused by differences in contraction were "frozen." This temperature turns out to be, in many cases, actually about an average temperature between the upper annealing temperature and the lower critical point, but this would depend on the actual firing schedule. It is a fair approximation for the purpose of explanation here to use as the "freez-

ing temperature" the average between the two extreme temperatures of the annealing range to compare fluxes of similar compositions but of somewhat different coefficients of expansion. If the expansion curve for a flux whose coefficient of expansion is smaller than the one that produced the ceramic color which "matched" the glass is superimposed on the curve for the expansion of the glass so that the curves cross at the average annealing temperature, the two curves cross again at some temperature above room temperature. This ceramic color would therefore actually be in compression when fired to the glass and cooled to room temperature. Similarly, if the expansion curve for a flux whose coefficient of expansion is larger than the first is superimposed on that of the glass so that they intersect at the average annealing temperature of the flux, the curve for the flux falls below that of the glass at all lower temperatures down to room temperature and if a color made from such a flux were fired to this glass the ceramic color would be in tension and a compression would appear on the glass under the color.

An explanation is thus obtained as to why, even though several ceramic colors have coefficients of expansion which are lower than that of the glass on which they are applied, some may produce a tension in the glass under the color, others may produce a compression, and one may match the glass exactly.

VI. Summary

A considerable amount of work has been done to determine the cause of the weakening effect of some applied color labels on the strength of glass bottles. The strength of the bottles was found to be unchanged after the label had been applied except when (1) the difference in thermal expansion between the bottle and the applied color label was such as to produce a tension strain in the label or (2) the applied color label was so unstable that it devitrified during the firing process, crystallizing out a silica-rich phase and leaving a matrix consisting of a high alkali phase having a high thermal expansion. The difference in thermal expansion between the matrix and the glass gave rise to a tension strain in the applied color label.

It has long been recognized that tension strains on the surface of glassware are undesirable because they reduce the strength of the glass. The present work has affirmed this contention in the case where the outside surface is an applied color label. When the label is not in tension, the ware is as strong after the label has been applied as it was before.

A rapid method for determining the suitability of the applied color for use with a particular glass is suggested. It is also shown that an applied color label which contains lithia, if properly compounded, will not reduce the strength of the glass to which it is applied. A tentative explanation is presented of the factors involved during the decoration process which result in strains in the glass under the applied color label.

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